

DOE/NASA/1002-78/2

NASA TM-79067

REDOX FLOW CELL DEVELOPMENT AND DEMONSTRATION PROJECT CALENDAR YEAR 1977

(NASA-TM-79067) REDOX FLOW CELL DEVELOPMENT
AND DEMONSTRATION PROJECT, CALENDAR YEAR
1977 (NASA) 53 p HC AC4/ME A01 CSCI 10A

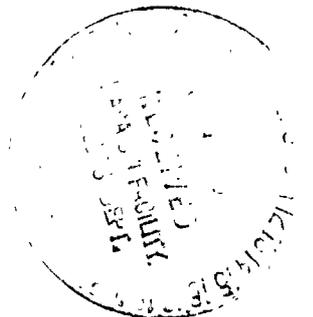
N79-24445

Unclas
G3/44 22089

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

Prepared for

DEPARTMENT OF ENERGY
Office of Energy Technology
Under Interagency Agreement E(49-28)-1002



DOE/NASA/1002-78/2
NASA TM-79067

REDOX FLOW CELL DEVELOPMENT
AND DEMONSTRATION PROJECT
CALENDAR YEAR 1977

National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio 44135

January 1979

Prepared for
U. S. DEPARTMENT OF ENERGY
Office of Energy Technology
Division of Energy Storage Systems
Washington, D. C. 20545
Under Interagency Agreement E(49-28)-1002

CONTENTS

	Page
EXECUTIVE SUMMARY	1
I. PROJECT OVERVIEW	6
II. MEMBRANE DEVELOPMENT	10
Introduction	10
Contract Efforts	12
In-house Efforts	20
III. FUNDAMENTAL ELECTROCHEMISTRY	26
Introduction	26
Contract Efforts	28
In-house Efforts	28
IV. CELL COMPONENT SCREENING	32
Introduction	32
Redox Couples	32
Electrodes	36
V. SYSTEM CONSIDERATIONS	42
System Studies	42
Materials Availability	45
Redox System Hardware	45
Redox System Projections	45
REFERENCES	48

EXECUTIVE SUMMARY

The NASA Lewis Research Center is conducting a research and development effort for the Division of Energy Storage Systems of the Department of Energy under NASA-DOE Interagency Agreement E(49-28)-1002, entitled "Redox Flow Cell Development and Demonstration Project." NASA began work on this effort in 1973 under internal sponsorship. Preliminary feasibility studies and laboratory experimentation were encouraging. United States Patent 3,996,064 was issued December 7, 1976 covering the novel features of the NASA concept of redox flow cells. In mid 1975 the Interagency Agreement was signed with ERDA which permitted an expansion of the efforts applied to this concept for the bulk storage of electrical energy. This report is the second in a series of annual reports covering the work performed as part of this Interagency Agreement. The long term goal of this project is to develop redox flow cell systems into a viable candidate for the bulk storage of electrical energy.

The redox flow cell concept involves the use of two fully soluble reduction-oxidation (redox) couples as the electrochemical reactants in flow cells that contain only inert electrodes and an ion exchange membrane which separates the reactant solutions. Storage tanks contain the majority of these solutions and pumps are used to circulate the negative solution and positive solution through the cells, which are assembled into stacks. Because of its design flexibility, in which storage capacity and power level can be sized independently, the redox system should be especially suited for operation on a weekly energy storage cycle in a utility environment or in a solar photovoltaic or wind application. Compared to a daily storage cycle, a weekly storage cycle is much more useful from a utility point of view since as much as 40 percent of the available energy for storage is generated over the weekend.

For the reporting period covering calendar year 1977 the main focus was placed upon the ferrous/ferric and chromous/chromic redox cell. The development of improved membranes and an electrode structure for use with the chromous/chromic couple in chloride solution was emphasized. The program directives from DOE require that attractive concepts for energy storage be evaluated as early as possible to assess their potential for development into viable commercial systems. For this reason only key issues that directly influence the fundamental feasibility of the overall redox concept were addressed. In the membrane area, efforts were focused on optimizing several new polymer systems in an effort to produce membranes that had reduced area resistivities and reduced rates of cross mixing of the reactive ionic species. Electrode materials were sought that would be more reversible for the chromium couple and would minimize rates of hydrogen evolution during recharge. Some system modeling and cost estimation was done to help direct the laboratory efforts.

Again this year significant improvements have been made in the areas of membrane properties and electrode performance and in understanding the electrochemistry of reactant solutions and the interaction of the system parameters that affect the projected cost of the overall system.

The function of the ion selective membrane in redox cells is to prohibit the passage of the reactive ions of the redox couples and yet permit the passage of nonreactive ions from the positive to the negative solution and vice versa. The parameters that are used to evaluate developmental membranes are the extrapolated half-life and the area resistivity. Several novel membrane systems (the copolymer of vinylbenzylchloride and dimethylaminoethylmethacrylate, and the copolymer of vinylbenzylchloride and either 2- or 4-vinylpyridine) were developed which employed monomers that contained ion exchange sites on both the backbone and crosslink portions of the copolymer. These yielded unprecedentedly high values for the crossover half-lives (~50 000 to >100 000 hr) and small diffusion rates, while still possessing reasonably low area resistivities (~5 to 10 $\Omega \text{ cm}^2$, measured in 0.1 N HCl). By going to thinner substrate material, thinner membranes (~0.1 mm vs 0.6 mm) were produced. The area resistivities were reduced by a factor of about three. Early attempts to produce even thinner membranes by depositing a skin of active material onto a porous supportive substrate have been encouraging. The potential also exists to reduce the resistance of standard membrane configurations by altering the formulation to produce a more open structure. The present goal is to produce membranes that will have the features listed in table I which also shows the progress made in the membrane area.

Electrochemical analytical techniques were employed as an aid in the development of suitable electrode structures on which the redox electrochemical reactions take place. They were also employed to help screen some of the potentially attractive redox couples, as well as to estimate electrochemical active areas of electrode materials. A graphite cloth obtained from Hitco Corporation of Gardena California, designated G 2252, displayed the best performance as a chromium electrode. Performance of the various electrode materials were evaluated in terms of the magnitude of the current during charging, and of the ampere hour efficiency from cycle to cycle. During the major portion of a standard charge cycle this Hitco material resulted in a charging current of approximately 5.0 mA/cm². This value is three times greater than any other carbon or graphite product examined, and is about 20 percent of the value deemed necessary for a fully practical cell. The average ampere hour efficiency over the course of 12 charge and discharge cycles were greater than 98 percent.

A number of other electrode materials are presently under investigation in actual redox flow cells as well as in a test apparatus that is specialized for

TABLE I. - IMPROVEMENTS IN MEMBRANE CHARACTERISTICS

Characteristic	1974*	1975	1976	1977	Goal
Membrane diffusion rate $\mu\text{gm Fe}^{+3}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$	1300	100	15	2	10-20
Membrane resistance, $\Omega\text{-cm}^2$	50	4 to 20	4 to 10	2 to 10	1
Resistance stability	Bad	Poor to fair	Poor to good	Poor to good	Good
Membrane thickness	0.6 mm	0.6 mm	0.6 mm	0.6 mm .12 mm <.10 mm	

*Off-the-shelf membranes.

the performance of electrochemical diagnostics (e.g., rotating disk electrode). Boron carbide has demonstrated encouraging results in terms of the ratio of current involved in recharging the chromic ion to that involved in the undesired side reaction of generating hydrogen. The chronopotentiostatic technique is being used in this study.

The sweep voltammetry technique was used to evaluate the relative reversibility of a number of redox couples. Compared to the $\text{Fe}^{+2}/\text{Fe}^{+3}$ couple in acidified chloride solutions, couples such as $\text{Cr}^{+2}/\text{Cr}^{+3}$, $\text{V}^{+2}/\text{V}^{+3}$ and $\text{V}^{+4}/\text{V}^{+5}$ were much less reversible. The couples $\text{Br}^-/\text{Br}_3^-$ and $\text{Cr}^{+2}/\text{Cr}^{+3}$ on B_4C electrodes were more reversible than were these same couples on carbon rod electrodes.

The combination of iron and titanium which was emphasized in most earlier work has been eliminated as a contender for a redox system due to the low overall voltage of this pair of couples. However, oxidized screens of tungsten and of tungsten alloyed with three percent rhenium (0.005 cm wire, 120 strands/in.) produced a much better electrode for use in titanium solutions. This material approximately quadrupled the power output of a standard iron/titanium cell.

The cell component screening and life testing aspects of this project are carried out as part of the requirement to evaluate new membrane formulations, new electrode candidates and experimental cell designs. Testing of this type has served the secondary purpose of revealing, at an early stage, system-related problems and characteristics. Redox flow cell test stands are gradually being adapted to perform specialty tests. One stand has been set up to evaluate the hydrogen evolution characteristics of various electrode structures. Another has been modified to facilitate the investigation of flow-through as well as flow-by electrodes. Several of the new improved membrane materials have displayed undesirable and as yet unexplained fluctuations in resistance when subjected to actual redox flow cell conditions. This apparent fouling of the membrane is reversible, and the initial resistance of the membrane is restored by rinsing the membrane in 1 N HCl solution. Specialty cells employing the same redox couple on both sides of the membrane ($\text{Fe}^{+2}/\text{Fe}^{+3}$ // $\text{Fe}^{+2}/\text{Fe}^{+3}$, etc) have thus far pointed to the $\text{Fe}^{+2}/\text{Fe}^{+3}$ couple as the source of this problem. Certain other membrane formulations are relatively free from this phenomenon.

There has not been much in the way of small scale system tests as such. Most of these tests have as their primary objective either membrane evaluation or electrode tests. Systems consisting of approximately 1.0 A hr capacity of iron/chromium, iron/titanium or bromine/titanium have been cycled. The iron/chromium cells, as well as the bromine/titanium cell,

consistently yielded ampere-hour efficiencies ($A\text{-hr out}/A\text{-hr in} \times 100$) of 98 percent. The iron/titanium cell had lower values, ranging from 98 percent near the start of cycling to about 80 percent after 27 cycles. The former two cells had 12 and 7 charge/discharge cycles, respectively, prior to the completion of testing. The titanium electrode in the Fe/Ti cell was the tungsten-3 percent rhenium screen, which has a more severe hydrogen evolution problem on charge, compared to the graphite foam electrode used in the Br/Ti cell.

Cell imbalance problems typically arise in electrochemical cells when the effects of irreversibilities or undesired side reactions accumulate over a number of charge and discharge cycles. With redox flow cells the problems are somewhat simplified since there is but one reservoir for the negative reactant and one for the positive reactant. This permits balancing to be performed at the system level instead of the single-cell level. The most common cause of cell imbalance would be the coevolution of hydrogen at the negative electrode during charge. Tests are just starting to measure this coevolution rate and to actually rebalance the cell by electrochemically reacting the hydrogen in a cell with a commensurate amount of ferric ion.

The System Study contract with Exxon Research and Engineering Co., Linden, New Jersey was completed. A bibliography was compiled containing over 800 references covering data on utility operation, electrochemical storage systems and nonelectrochemical storage systems. A definition of storage applications and utility requirements was developed to the extent possible, considering the state of maturity of this general topic and the sensitivity to site-specific and utility-specific factors. Several redox models were set up on a computer and daily and weekly load cycles were evaluated. The effect of system variables, e. g., current density, cell voltage and component costs on the overall system cost was evaluated. After certain adjustments in several component costing subroutines and program logic were made, useful information pertaining to "cost centers" was obtained. System cost projections ranged from ~250 \$/kW to 600 \$/kW for a 5 hr storage system. This range is still within the range of break-even cost projections for energy storage for utility service. The redox concept of course is more attractive for the longer duration storage applications. The costing of redox systems might be more aptly stated in terms of a certain cost per kilowatt for the power conversion and power processing equipment plus a small incremental cost for the storage and reactant parts of the system. A figure of 140 to 180 \$/kW plus 10 to 12 \$/kW-hr is the present estimate for the system cost in a mature industry.

The availability, cost, annual production rate and estimates of world and U. S. resources were determined for source-ores for redox reactants. Further, the impact on the annual world production of these ores, to provide reactants

for 100, 100 MW-hr redox installations, was calculated. For example 1.9 percent of the yearly world production of chromium would be used in producing 10 000 MW-hr of chromium solution. The ore price for chromium in 1976 was 30 ¢/1000 A-hr.

I. PROJECT OVERVIEW

The calendar year 1977 research and development efforts associated with the Redox Flow Cell Development and Demonstration Project are described. The project is being conducted by the NASA Lewis Research Center under Interagency Agreement E(49-28)-1002 with the U. S. Department of Energy (DOE). This project is part of the Electrochemical Energy Storage Program directed by the Division of Energy Storage Systems of DOE.

The long-term objective of this project is to develop and demonstrate a redox flow system of sufficient energy capacity to provide useful operating experience and preliminary cost data as basic input for the design and construction of large commercial systems. For the near term, attention is being focused upon the key technology issues that will determine the fundamental feasibility of the overall redox concept. These issues are:

1. Development of membrane materials with increased selectivity (to reduce the rate of cross mixing that takes place within the cells) and reduced resistance to the transport of nonreactive ions across the membrane.
2. Development of an electrode material for use with the chromous/chromic couple.

Quantitatively, the technical goals for the project were to produce membranes with calculated half-lives for crossmixing of greater than 3000 hr and with resistivities of less than 10 Ω -cm. The goal for electrode performance was to produce 10 W/ft² of electrode area.

A number of studies and projections have been made to show the value of energy storage as part of an electric utility generation mix. In the final analysis, storage for electric utilities will be accepted or rejected on the basis of its impact on the economic of operation of the utilities. A viable storage system will permit the utilities to increase the load factors for their more-efficient baseload generating equipment, and will reduce the demand on older, less-efficient equipment and peaking turbines. Storage capability will also permit the utilities to increase their baseload capacities to optimum levels and to phase out, or refrain from purchasing, less-efficient equipment.

In a study performed for ERDA by the Public Service Electric and Gas Company (ref. 1), load characteristics of 199 U. S. electric utility systems were analyzed. These systems represent 90 percent of the total installed

capacity and 95 percent of the net energy generated in the United States. From these 199 systems, 8 were selected as being most representative of the utility industry, based on system size, peaking season, annual load factor, daily load shape, generation mix, and geographic location. For each of these 8 representative systems an optimum baseload capacity was identified which would provide the maximum amount of off-peak (storable) energy for meeting peak requirements. The analysis reveals that the theoretical maximum amount of peak energy which could be supported by off-peak storage is about 10 percent of the annual energy production. For the study year of 1971, this would amount to 160×10^9 kW-hr. On a practical level, assuming a weekly storage cycle and 75-percent electric-to-electric conversion efficiency and disregarding the off-peak energy which does not occur on a consistent basis during the entire year, the amount of supportable peak energy becomes 5 percent of annual energy generation, or 80×10^9 kW-hr nationally. Similarly, the discharge power capacity for energy storage on a typical system theoretically is 20 percent of the annual system peak power. For 75-percent conversion efficiency and a weekly cycle this discharge power capacity becomes 17 percent of the annual peak. When consideration is given to daily cycle operation under the previously-defined practical conditions, the amount of supportable peak energy falls from 5 percent to 2 percent of annual production, and the discharge power capacity falls from 17 percent to 12 percent of the annual peak. Because the energy storage section and the power generating section of a redox system can be independently sized, such a system is more amenable than conventional batteries to being cost-efficiently designed for a weekly duty cycle. Thus, a redox system can be more cheaply adapted to take advantage of the higher energy and power possibilities for the weekly cycle.

Solar and wind turbine generation of electric energy, because of their intermittent output will require a storage capability. However, the economics of integrating storage devices into these systems is not as well defined as for utilities. It may be that necessity will allow a premium to be paid for storage devices with these energy systems.

Among the various technologies contending for an electric energy storage role, one of the more attractive is electrochemical storage. Of course, no battery system of the size necessary for utility applications has ever been assembled. Present batteries, having well-developed technologies, may be troubled by cost, depth-of-discharge limitations, electrode morphology changes, and cycle-life limitations. Economic evaluation of advanced batteries is made difficult by the rudimentary state of the art.

Redox systems are not batteries in the traditional sense. Although some electrochemical technology is common to both, the redox system has a much

greater similarity to fuel cell systems. The redox system being developed at Lewis is referred to as a "two tank" system because each reactant is continuously recirculated between its respective storage tank and the power-generating module. The higher-than-stoichiometric flow rates enhance mass transport at the redox cell electrodes. Also, the fact that the reactants are only fractionally depleted on each pass through the cells permits higher power densities than can be achieved with single-pass (four tank) systems. Because there is no phase change as a redox couple is charged or discharged, there are no inherent depth-of-discharge or cycle-life limitations for a redox system. Materials problems are minimized because operating temperatures are mild. An additional advantage over conventional batteries is that the energy storage capacity and the power generation capability of a redox system can be independently sized, permitting optimum reactant utilization and cost efficient design for weekly cycle operation. Also the modular character of redox system components will permit efficient expansion to meet evolving power levels and load factors.

In theory, the major drawback to a redox system is that, because of the modest energy density of its reactant solutions, it is a high-volume system. This will be reflected in costs for land and tankage. In practice, the problems encountered at Lewis revolve around the development of a suitable membrane and an adequate negative reactant/electrolyte/electrode combination for the redox system. Most of the redox project effort during 1977 has been directed toward these problems. These efforts, carried out both in-house and under contract, have had notable success. Of particular significance are the improvements in the membrane resistivities and membrane crossmixing half-lives. The membrane development is done under contract by Ionics, Incorporated of Watertown, Massachusetts. These membranes, which in general are fabric supported, crosslinked polyelectrolyte ion exchange membranes, have shown further advancements in both of these aforementioned properties. The novel technique of using crosslinking agents that contain ion exchange sites in addition to those on the backbone polymer chain has produced these advancements. The technique of applying thin films of membrane materials onto porous supportive substrates is also showing promise of even further reductions in membrane resistance and crossmixing rates.

The positive couple that received the most attention was the ferrous/ferric couple. A few experiments were carried out with the bromide/bromine couple. The majority of the negative couple work was centered around the chromous/chromic couple. This couple has an attractive voltage (1.2 vs $\text{Fe}^{+2}/\text{Fe}^{+3}$) but is not nearly as reversible as the ferrous/ferric couple. This lack of reversibility leads to poor ampere-hour and watt-hour efficiencies. Electrode structures that may catalyze this reaction are under investigation. A catalytic surface of oxidized tungsten has been found which eliminates the voltage loss

problems that were associated with carbon and graphite products when used as electrodes for the titanous/titanyl couple. The screening efforts also examined several vanadium-based couples as well as the iron oxalate couple.

A contract effort with Giner Incorporated of Waltham, Massachusetts has augmented the inhouse efforts directed towards the chromous/chromic couple. During this reporting period work related to the solubilities of chromous chloride and chromic chloride as a function of hydrochloric acid concentration was carried out.

The search for a suitable electrode structure for the chromium couple has resulted in the testing of a variety of felts, foams and cloths made into carbon and graphite forms. Further, the performance of several metal carbide and nitride surfaces have been tested for catalytic behavior. Work in the electrode evaluation subtask has employed electrochemical diagnostics to estimate the surface area, the relative rates of unwanted side reactions and the degree of reversibility exhibited on each surface. The deposition of potentially catalytic surfaces onto porous substrates has also been tried.

The System Study contract performed by Exxon Research and Engineering Co., Linden, New Jersey was completed. Much useful information was derived from this contract, including detailed definitions of possible electric storage applications and the requirements imposed by these applications on candidate storage systems. Three redox system models were developed and programmed for computer solution. These include the Stage 1 model for daily cycles and time-averaged operational parameters, the Stage 1.5 model for weekly cycles and time-averaged parameters, and the much more sophisticated Stage 2 model which calculates time-dependent solutions.

It was our opinion that the component costing subroutines in these programs were generating excessively high values. We modified them to give costs that are judged to be more realistic. The correctness of this judgment has been reinforced by an independent component cost analysis performed by an engineering design contractor. The Stage 1 model with the modified costing subroutines and using conservative parameter values predicts redox system costs around \$400/kW. Less conservative, but probably attainable, parameter values reduce this cost to \$220/kW.

Other topics that were investigated included the availability and cost of raw materials for the reactants for redox cells, and sources, production rates, estimates of mineral reserves etc. for these materials.

The similarity between redox systems and the equipment used in commercial electrodialysis equipment has permitted an estimate to be made of the projected costs of future redox equipment.

The effort for the next reporting period will be centered around making yet another generation of advancements in the membrane and the electrode

structures. These improvements will be incorporated in a short stack of redox flow cells that will be considerably larger than the small cells that have been used in the screening and cycle life testing. This short stack will be cycled to demonstrate an interim stage of system feasibility.

II. MEMBRANE DEVELOPMENT

Introduction

The membranes used in redox flow cells are ion exchange resins that are fabricated as thin sheets reinforced by a layer of woven fabric. The resin itself is a copolymer of the constituents which form the backbone and the crosslink parts, respectively, of the membrane chemistry. Figure 1 schematically shows such an ion exchange resin. The following parameters determine the properties of the ion exchange membranes:

1. Backbone monomer
2. Crosslink monomer
3. Crosslink density
4. Fraction of nonpolymerizable material in the membrane

By incorporating variations in the above listed parameters a wide spectrum of membrane characteristics are possible. The process of optimizing these membranes for the redox application is based on the application of the principles set forth by Donnan in regards to ion exclusion from membranes. In essence, the Donnan Exclusion Principle suggests that to prohibit the passage of cations through a membrane, the membrane should contain cation charge sites. The higher the number density of these sites, the more selective the membrane would be. Further, to take full advantage of the ion exclusion, the effective hole size must be as small as possible, yet not hinder the passage of the anions. The selectivity and the conductivity of a membrane are of equal importance, and thus efforts to optimize the membrane are measured by evaluating both factors. (Due to the very small size of the hydrogen ion it is impossible to preclude its passage across the membrane.)

The number density of charge sites that are contained within a membrane is measured by its ion exchange capacity (IEC) in milliequivalents per dry gram of material (MEQ/DGM). Due to the affinity for water possessed by the ion exchange sites, membranes with high capacities are prone to swelling. Unless adequate crosslink density is incorporated into the structure, membranes with high IEC are very weak. Since the most selective membranes result from high IEC materials, membranes must be optimized for this factor. In properly functioning membranes (free of defects) only a very thin layer of resin is required to actually accomplish the exclusion of ions. Thus, reductions

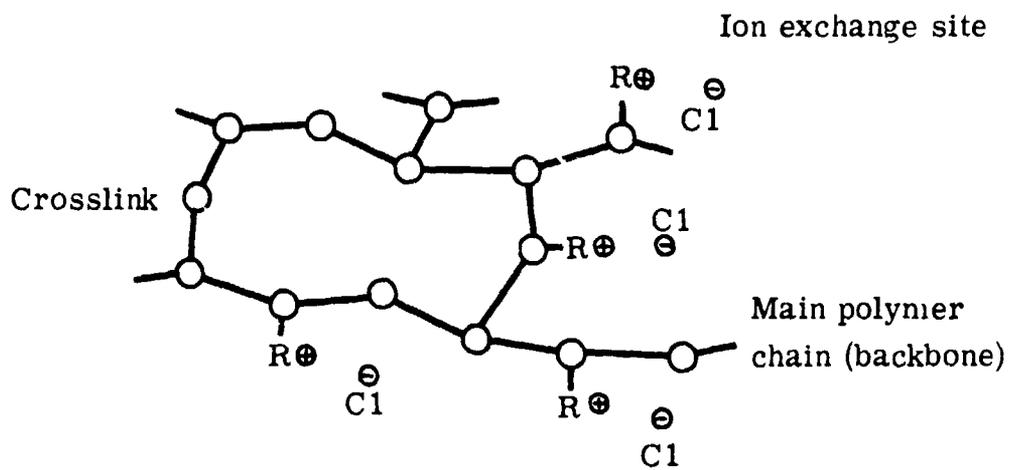


Figure 1. - Generalized structure of fabric supported, cross-linked polyelectrolyte ion exchange membranes.

in substrate thickness should result in reductions in resistance to the passage of anions and hydrogen ions across the membrane without appreciable reductions in the membrane selectivity. As stated earlier, selectivity results from a combination of the effects of ion exchange capacity and the effective diameter of the "holes" through which the ions pass from one side of the membrane to the other. The membrane engineering that is applied to adjust these "hole" sizes is not well understood but is affected by such things as the polymerization conditions, the solvent used, and the fraction of nonpolymerizable material that is contained in the mixture when it is polymerized. Typically, the fabric support is dipped into the formulation and then placed between glass sheets prior to the initiation of polymerization. Finished membranes are then stripped away from the glass sheets. Once the membranes are properly equilibrated with water they must remain wetted to prevent any cracking which may otherwise result.

Membrane thickness may be varied by using cloth substrates of various thicknesses. With the thinner cloths, care must be exercised to insure complete wetting of the cloth by the mixture of monomers and solvent. A further method to produce highly selective low resistance membranes is to use a porous plastic film as the substrate for a thin layer of ion exchange resin. This ion exchange layer results from a spray or dip application of the formulations of the type previously described. This type of membrane, referred to as a composite or skin membrane, could be mass-produced using various spray, evaporate and bake steps on a continuous sheet of film substrate.

A. Contract Efforts

The membrane development program at Ionics, Inc. entered a second follow-on phase during September 1977 (Contract DEN3-1). The initial contract effort was performed in 1974 to 1975; the second contract extended from July 1976 to August 1977 and the results of this effort are highlighted in this report.

The contract program included three major tasks:

- (1) Synthesize and screen new or unproven membranes for the redox cell application. Screening parameters included ion-exchange capacity, water content, resistance and ferric ion permeation rates.
- (2) Optimize six promising candidate membranes for increased selectivity (minimal ferric ion transfer), minimal resistance, and enhanced durability in the redox environment.
- (3) Scale-up of membrane fabrication for optimized systems, and a detailed characterization of electrical and physical properties of the membranes.

During this reporting period, thirteen different chemical systems were screened as membrane materials. Of these, six were chosen as candidate membrane materials and were optimized in Task 2. These materials were evaluated on Dynel cloth supports (giving membranes nominally 0.6 mm thick). Some of the systems were compatible with thinner cloth supports (permitting membrane thicknesses of 0.1 to 0.25 mm); however, membrane properties were not as reproducible in the thinner configuration.

The five most promising candidate membranes in Ionics' screening tests were (in descending order of overall performance):

(1) CP4L-A2 (a copolymer of 4-vinylpyridine and vinylbenzylchloride). This system exhibits several advantages. It has very high ion exchange capacity, which results in low resistance and exceptionally low ferric ion transfer. It exhibits excellent stability in the redox environment. It is a two-component, self-crosslinking type system which facilitates membrane fabrication; and it is compatible with the thin cloth substrates.

(2) A3L-B7 (a copolymer of 2-vinylpyridine and divinylbenzene). This system also exhibits several advantages. It has an intermediate ion exchange capacity, but still has very low ferric ion transfer and excellent stability in the redox environment. It, too, is fabricated in a single step and is compatible with the thinner substrates.

(3) 103 QZL-B10 (a copolymer of divinylbenzene and vinylbenzylchloride post-aminated with trimethylamine). This membrane is an improved version of a commercial membrane manufactured by Ionics Inc. The inherently lower exchange capacity and the multi-step synthesis required make it less desirable than systems (1) and (2).

(4) CD1L-A5 (a copolymer of vinylbenzylchloride and dimethylaminoethylmethacrylate). This system offers the same advantages as system (1) except that it is not as stable in Fe and Cr halide solutions at 80° C.

(5) B2LDT-B2 (a copolymer of vinylbenzylchloride and divinylbenzene, post-aminated with diethylenetriamine) This system performed well at intermediate exchange capacities, but has a multistep synthesis as does system (3) and is not as desirable as systems (1) and (2).

These membranes all showed significant improvements in performance compared to prior state-of-the-art membranes. Table 2 gives selected physical properties of these membranes as measured by Ionics. The most significant aspect of these data is the exceptionally low ferric ion transfer rates attained. These values represent an improvement of approximately three orders of magnitude compared to the prior state of the art. This exceptional level of selective ion transfer is reflected in the performance of redox cells employing these membranes (discussed below). Membrane resistance was also decreased during this period by a factor of 2 to 3.

TABLE 2. - PHYSICAL PROPERTIES OF IONICS MEMBRANES

Membrane	Ion exchange capacity, meq/g	Water content, percent	Resistance, ^a Ω -cm ²	Ferric ion transport rate, mg Fe/mF
CP4L-A2	5.3	32	1.8	0.004-0.008
A3L-B7	3.6	32	9.1	0.001-0.002
103 QZL-B10	2.2	25	10.6	0.002-0.003
CD1L-A5	4.1	31	6.7	0.005-0.008
B2LDT-B2	3.5	30	8.7	0.001-0.002
Interim goal	---	--	----	0.007

^aMeasured by contact probes after equilibration in 0.1 N HCl.

A complete review of the contract efforts on these membranes may be found in the contractor's final report (ref. 2). A group of selected tables from that report are included here. Most of the terms used in these tables are self explanatory with the exception of the term used to measure the cross diffusion characteristic of the membranes. The test setup which is outlined in full in reference 2 impresses a migration potential on ferric ions. This driving force is such that the iron ions would tend to leave a circulating solution of ferric chloride and pass through the membrane in question into a second circulating solution of hydrochloric acid. The total ionic flow is determined by measuring the dc current, and the contribution of the ferric ions to this flow is determined by analyzing the hydrochloric acid solution. The term "milligrams of iron per millifaraday" is thus related to the transference number of ferric ions.

Table 3 is a summary table of the information gathered for the CD1L system. This chemistry is one which employs an ion exchange group as part of the crosslinking agent. Several different variations of the volume fraction of nonpolymerizable solvent and the molar fraction of crosslink monomer were examined. The iron transfer P_{Fe}^+ , and the area resistivity R_p^c , represent the characteristics of primary interest. Table 4 contains the same type of information for the CP4L system. Only those films for which the nonpolymerizable fraction was 0.25 are covered here. Table 5 contains a listing of various membranes and their area resistivities after soaking in several different concentrations of hydrochloric acid.

The membranes at the top of the table are those having the more open structures and lower IEC's. Because of these characteristics, these membranes have, at low HCl concentrations, high resistivities since the low IEC's do not enhance Cl-transfer. However due to their open structure they pass protons quite easily and are thus very sensitive to increases in acid concentration. Conversely, the high-IEC, low porosity membranes (CD1L and CP4L) transport Cl-ions easily, even at low acid concentrations, but are less sensitive to increases in the acid concentration because the protons tend to be excluded from the transport process. The consequence of eliminating highly mobile hydrogen ion from the solution is illustrated in table 6 where the area resistivities of these membranes are measured as a function of the sodium chloride concentration. As in the previous table the more selective membranes are less effected by the change in ionic environment than the less selective membranes.

The most recent program (initiated in September 1977) directly addresses the need for lower membrane resistance. Preliminary data have revealed two promising approaches: (1) coating very thin films of ion exchange resins (in particular systems CP4L and A3L) on very porous substrates; and (2) fabrication of the best membranes discussed above in configurations having greater

TABLE 3. - CD1L MEMBRANE SYSTEM - SUMMARY

[Copolymers - vinylbenzylchloride, dimethylaminoethylmethacrylate fabric backing - woven Dynel, film thickness - 0.60 mm.]

Membrane	Synthesis method	Monomer formulation		Fe transfer P_{Fe}^+ mg Fe/mF $\times 10^{-3}$	Resistivity R_p^C in 0.1 N HCl (Ω -cm 2)	IEC meq/dgm			H $_2$ O content percent
		f_{NP}	f_{MR}			Total	Strong	Weak	
CD1L-A1	1 step	0.30	1.5	17	9.3	4.44	2.28	2.16	42.4
CD1L-A2	1 step	.30	2.0	41	5.2	4.26	2.19	2.07	39.4
CD1L-A3	1 step	.30	2.5	21	5.2	4.04	2.61	1.43	37.3
CD1L-A4	1 step	.30	3.0	49	5.2	5.06	2.50	2.56	40.1
CD1L-A5	1 step	.25	2.0	8	5.2	4.18	2.87	1.21	32.9
CD1L-A6	1 step	.20	2.0	14	6.2	4.16	2.27	1.89	35.1
CD1L-A7	1 step	.50	2.0	--	---	4.39	2.34	2.05	49.0
CD1L-A5H	2 step	.25	2.0	4	6.5	4.03	2.25	1.78	31.2
CD1L-A6H	2 step	.20	2.0	5	7.3	4.29	1.68	2.61	32.1
CD1L-A8H	2 step	.40	2.0	--	---	4.18	1.88	2.30	42.0

f_{NP} = volume fraction of nonpolymerizable solvent

f_{MR} = molar ratio DMAEMA/VBC

P_{Fe}^+ = Fe transfer at CD = 60 mA/cm 2

TABLE 4. - VARIATIONS IN CP POLYMER SYSTEM - PHYSICAL AND CHEMICAL PROPERTIES OF MEMBRANE

[Monomers - vinylbenzyl chloride, 4-vinylpyridine $f_{NP} = 0.25$, fabric support - Dynel, membrane size - 5 in. by 5 in.]

Membrane sample	Vinyl pyridine monomer	Molar ratio, M_R VP/VBC	IEC (meq/dgr)			Percent H_2O	R^c in 0.1 N HCl ($\Omega\text{-cm}^2$)	Fe transfer, P_{Fe}^+ (mg Fe/mF/10 ⁻³)	Physical condition of film		
			Total	Strong	Weak				Surface erosion	Leak	Other
CP4L-A1	4 VP	4	6.32	2.06	4.27	42.9	2.4	---	Severe	Few pinholes	Very flexible
CP4L-A2	4 VP	2	5.09	2.85	2.24	26.9	4.2	5-9	Moderate	Few pinholes	Few cracks
CP4L-A3	4 VP	1.5	4.67	2.79	1.88	23.7	5.8	3-4	Slight	Few pinholes	Few small cracks
CP4L-A4	4 VP	1.3	4.39	2.77	1.62	21.2	6.5	2-3	Slight	Few pinholes	Few small cracks
CP4L-A5	4 VP	1.2	4.21	2.63	1.58	19.8	6.5	Leaks on testing	Slight	Few pinholes	Polymer fragile develops cracks with slight pressure
CP4L-A6	4 VP	1.0	3.71	2.30	1.41	23.4	10.2	---	None	Few pinholes	Slightly stiff
CP4L-A2 ¹	2 VP	2	4.63	2.25	2.38	31.4	---	---	None	Few pinholes	Mod. flexible
CP4L-A2 ¹	4 VP	2	5.30	2.94	2.36	31.6	1.8	4-8	None	None	Flexible
CP4L-A3 ¹	4 VP	1.5	4.61	3.14	1.47	31.2	4.6	2-3	None	None	Dk. br. flexible

¹On modacrylic woven backing - film thickness = 0.25 mm.

TABLE 5. - MEMBRANE RESISTIVITY AS A FUNCTION OF HCl CONCENTRATION

[Method of meas. - liquid junction, cell cross sectional area - 1.36 cm^2 , meas. frequency - 1000 Hz, temperature = 25° C

Membrane	Film thickness, mm	Backing fabric	Area resistivity R^j , in HCl ($\Omega\text{-cm}^2$)				Resistance ratio $R_{0.1}/R_{6.0}$	
			0.1 N	0.5 N	1.0 N	2.0 N		6.0 N
103 QZ1-B2	0.60	Dynel	13.1	6.80	4.17	3.03	2.06	6.4
103 QZL-B10	.60	Dynel	15.1	9.6	6.40	4.16	3.26	4.7
103 QZL-B10	.27	Teflon	6.81	4.24	2.63	1.55	1.13	4.8
A3L-B7	.60	Dynel	15.1	10.0	6.45	5.28	3.26	4.7
A3L-B7	.27	Teflon	8.59	5.55	3.75	2.23	1.85	4.6
A3L-B7	.15	Polypropylene	11.98	-----	3.17	-----	-----	---
A3L-B7	.25	Polypropylene	9.01	-----	3.60	-----	-----	---
B2LDT-B2	.60	Dynel 183	12.0	10.1	7.72	6.43	3.54	3.4
B2LDT-B2	.27	Teflon	6.53	5.17	4.19	3.03	2.03	3.1
CD1L-A5H-10	.60	Dynel	6.80	5.75	4.19	3.79	2.96	2.3
CD1L-A5-3	.11	Modacrylic	3.75	3.00	2.50	2.15	1.58	2.4
CP4L-A2	.23	Modacrylic	2.39	2.50	2.15	1.80	1.61	1.5
Solution resistance (Ω)			10.9	3.2	2.10	1.68	1.37	8.0

TABLE 6. - MEMBRANE RESISTIVITY AS A FUNCTION OF NaCl CONCENTRATION

[Method of measuring liquid junction, cell cross sectional area = 1.36 cm^2 ,
 meas. frequency - 1000 Hz, temperature = 25° C.]

Membrane	Film thickness, mm	Area resistivity R^J , in NaCl ($\Omega\text{-cm}^2$)					Resistance ratio R0.1/R5.0
		0.1 N	0.5 N	1.0 N	2.0 N	5.0 N	
103 QZL-B2	0.60	12.3	11.5	9.28	7.39	5.64	2.2
103 QZL-B10	.60	16.2	14.4	12.8	10.5	8.61	1.9
A3L-B7	.60	15.9	14.4	12.5	10.9	8.87	1.8
B2LDT-B2	.60	11.3	11.2	10.2	9.06	8.36	1.4
CD1L-A5H-10	.60	6.20	6.66	6.26	5.89	5.90	1.05
CD1L-A5-3	.11	3.87	3.64	3.44	3.34	3.60	1.08
CP4L-A2	.23	2.18	2.58	2.77	2.60	3.47	.63
Solution resistance (Ω)		28.3	8.82	5.41	3.64	2.68	10.6

(but controlled) porosity to enhance conductivity with minimal sacrifice of selectivity. Only preliminary data were collected prior to the conclusion of the CY 1977 cutoff date for this report.

B. In-house Efforts

The in-house work done in the membrane area deals primarily with evaluation of membranes that were produced as a result of the Ionics Inc. contract. The two membrane characteristics that are of interest are a measure of the cross diffusion rate of the cations and the ease by which anions and hydrogen ions can move through the membrane. Also of interest is the change of these parameters with time. Selected membranes that have undergone certain life tests are returned to the manufacturer for post-test evaluation. Some of the in-house tests complimented those carried out by the contractor while others used different test procedures to measure the two characteristics of interest—the cross diffusion rates of metal cations and the area resistivity to flow of anions and hydrogen ions. Life tests in small redox systems were used to evaluate various membranes in the actual environment of interest. In this setting, such factors as osmotic effects and changes in membrane resistivity and selectivity could be observed. These results were then factored into further membrane optimization attempts.

The routine tests performed on experimental membranes delivered for evaluation were static diffusion tests and area resistivity. The static diffusion tests were conducted as follows: A one molar chromium or iron solution was placed on one side of a membrane that was clamped between two small (3/4 in. diameter by 1/2 in. deep) cavities. The other cavity contained a hydrochloric acid solution of the same concentration as in the chromium or iron solution but contained no other cations. Lucite blocks were used for these cells and thus permitted observations to be made of the rate of diffusion into the dilute acid solution. After a predetermined length of time the dilute acid solution was sampled and analyzed by atomic absorption techniques. The better membranes underwent such minor cross diffusion during this test time, that the results of the chemical analyses were used to calculate a cross diffusion rate ($\mu\text{g/hr/cm}^2/\text{mol/liter}$) without needing to correct for any loss of gradient.

The area resistivity of each membrane was measured by presoaking the membrane in either 1.0 or 2.0 normal hydrochloric acid and then placing the membrane between electrodes of the type used in redox cells. A one thousand cycle ac bridge was used to make the measurement, which was then corrected by subtracting the resistance of the cell with no membrane included. Table 7

TABLE 7. - SUMMARY OF DATA AND RESULTS FROM EXPERIMENTAL MEMBRANES

Membrane	Diffusion tests						Resistance tests		
	In-house (static) $\mu\text{g}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$			Ionics $\mu\text{g}/\text{mF}$	In-house (cycling) $\mu\text{g}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$		Ionics resistivity $\Omega\text{-cm}^2$	Resistance stability cycling - Fe/Cr system cell resistance- Ω	
	Fe ⁺³	Fe ⁺²	Cr ⁺³		Fe ⁺³	Fe ⁺³		Cr ⁺³	0.1 N HCl
				Fe ⁺³			Cr ⁺³		
A3L-A52	7.75	-----	5.99	11-25	55.5	3.30	----	1.00	2.07
A3L-B7	13.38	-----	6.34	8-13	3.0	<1	15.4	1.01	1.50
103 QZL-B10	19.37	-----	12.32	10-20	34.4	14.6	15.4	1.10	2.60
103 QZL-A23	64.44	-----	51.76	12-40	21.2	6.72	-----	.78	1.04
103 QZL-B2	76.06	-----	57.04	28-46	-----	6.23	13.1	.85	1.78
CD1L-A5H10	3.17	5.63	.35	5-8	-----	3.63	6.5	.91	1.56
CD1L-A5H2	5.32	-----	2.23	-----	4.23	3.36	-----	-----	-----
CD1L-A5-3	14.08	9.86	3.52	7-8	<1	2.58	2.9	.80	1.5
CP4L-A3-3	.70	.70	.07	1	<1	1.16	4.6	.95	1.92
CP4L-A3-2	2.11	2.11	.70	2-5	<1	4.47	5.9	1.00	1.91
CP4L-A3-1	.70	1.41	.04	2-3	<1	<1	4.6	.94	2.32
CP4L-A2-1	5.63	2.82	1.41	4-9	<1	5.28	1.6	1.06	1.79

is a compilation of the tests performed on membranes evaluated during this reporting period.

The main factor to note is the consistently lower rates of cross diffusion of the chromium ions in comparison to the iron ions. Also the absence of a one-to-one relationship between the cross diffusion parameter as measured by Ionics, Inc. and the cross diffusion parameter as measured in-house.

In-house studies were also carried out to evaluate the time-related changes of the area resistivity and the selectivity. The method used to investigate the selectivity variations was to run a membrane in an actual redox cell for several weeks and then analyse the resultant redox solutions for cross-mixed reactants. Table 7 shows a typical set of results. Because of the good correspondence of the results from the two measurement techniques, long-term testing was abandoned in favor of the static diffusion tests for the screening type tests.

Stable area resistivities were not found in all membranes tested. Figure 2 depicts the two general types of time-dependent behavior of the internal cell resistance, which includes the membrane resistance. In certain cases the resistance would increase and reach a stable value, while in others there would be a prolonged and steady resistance rise. This increase is due to a fouling of the membrane and, in particular, a reversible fouling since membranes washed in hydrochloric acid solutions return to their original resistance value. Tests in cells that contained like redox couples on both sides of the membrane revealed that the iron species are the ones responsible for this increase in membrane resistance. A series of these tests summarized in table 8 shows the effects measured in iron/iron cells using various membranes. In general, the more open membranes (higher cross diffusion parameters) are less prone to significant increases in the area resistivity. The values tabulated here are total cell internal resistance, so the actual percentage change of membrane resistances would be higher than appears on this table.

A series of membranes from six different systems was prepared by Ionics, Inc. in an attempt to reduce membrane resistance by using thinner substrate materials. Teflon, polypropylene and modacrylic fabrics were compared with the standard substrate fabric, Dynel 183. Results of static diffusion tests for Fe^{+3} and Cr^{+3} are given in table 9. The Teflon and polypropylene supported membranes permitted more Fe^{+3} and Cr^{+3} diffusion than the Dynel or Modacrylic. This is attributed to the nonwetting characteristics of Teflon and polypropylene allowing voids between the substrates and resins as polymerization occurs. Resistance measurements on the 103QZL-B10 membrane on Teflon was considerably lower than on the Dynel 183. This is attributed to the greater contribution of H^{+} to the conductivity because of the more open structure as previously discussed.

Resistance increase indicates gradual fouling of charge sites or plugging of pores. (Acid flush restores original resistance value)

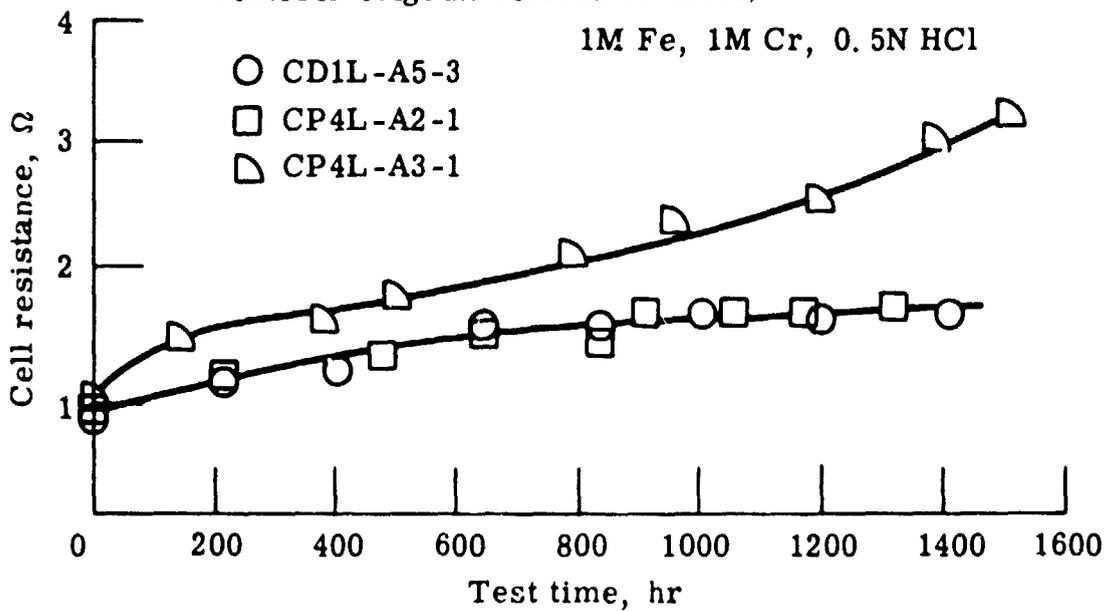


Figure 2. - Resistance stability of improved membranes in an iron/chromium cell.

TABLE 8. - SUMMARY OF DATA AND RESULTS FROM TRADITIONAL EXPERIMENTAL MEMBRANES

Membrane	Selectivity, $\mu\text{g/hr/cm}^2/\text{m/l}$	Resistivity, $\Omega\text{-cm}^2$	Cell resistance stability, %				
			Initial, I	100 hr	Maximum, M	Rm/Ri	Test time, hr
CD1L-A5N	38	3.5	0.35	0.44	0.44	1.26	504
CD1L-A5H10	6	6	.57	.85	.86	1.51	406
A3L-B7N	74	4.2	.40	.51	.57	1.43	479
CP4L-A2N	15	3.3	.40	.54	.57	1.43	481
CP4L-A2P (thin)	3	3.5	.72	.97	1.10	1.53	541
CP4L-A3-M100	1	---	.65	1.43	1.73	2.66	668
CP4L-A3-2	2	5	.55	1.20	1.48	2.69	673
CP4L-A2-1	6	2	.38	1.10	1.40	3.68	668
Interim goal	20	2	----	----	----	1.20	----

TABLE 9. - EFFECT OF MEMBRANE SUBSTRATE ON Fe⁺³ AND Cr⁺³ DIFFUSION RATE

Membrane formulation	Substrate material	Approximate thickness, mills	Average diffusion rate $\mu\text{g}/\text{cm}^2/\text{hr}/\text{M}/\text{L}$		Resistivity in 0.1 N HCl $\Omega\text{-cm}^2$
			Fe ⁺³	Cr ⁺³	
103 QZL-B10	Dynel 183	22	26	19	10.6
103 QZL-B10	Teflon T010	12	213	87	5.5
103 QZL-B2	Teflon T010	12	169	140	5.5
A3L-96X	Dynel 183	22	3.9	<1	
A3L-96X	Polypropylene P030	12	51	18	
A3L-96X	Teflon T010	12	71	82	
CP4L-A3*	Modacrylic M-100	8	<1	<1	
CD1L-A5	Modacrylic M-100	8	-----	4.2	
B2LDT-B2	Teflon T010	12	-----	20	
A3L-B7	Teflon T010	12	-----	35	
A3L-B7	Polypropylene P030	12	-----	29	

* Representative results from previous tests of high selectivity membrane.

III. FUNDAMENTAL ELECTROCHEMISTRY

Introduction

The purpose for the selection and application of specific electrochemical diagnostic tests was to break down the polarization losses in a redox system into four categories, and to assess the relative contributions of each. The four categories of polarization are:

1. Ohmic, which comprises membrane, solution and electrode resistances,
2. Activation, which involves the electrochemical rates of reaction at the electrode surfaces,
3. Long-term mass transport processes (diffusion and convection) from the bulk solution across the thin diffusion layer to the electrode surface,
4. Short-term mass transport processes related to charging of the double layer.

The approach was essentially diagnostic and was not intended for the purposes of determining reaction mechanisms or the evaluation of rate constants and diffusion coefficients. Three methods of obtaining information are shown in figure 3.

The top graph is for the interrupter method. The graph displays voltage (E) vs time after the current is abruptly interrupted. The precipitous drop is ohmic (IR). Immediately following this is a region where the process is dominated by the interaction of double layer capacitance and activation polarization (K). This overlaps with short term diffusion effects (D). After a few hundred milliseconds and continuing for a time interval measured in minutes the long term diffusion and convection effects predominate. The change in voltage measures the magnitude of the polarization due to a given effect.

The center graph illustrates sweep voltammetry. In this method the electrode potential is varied linearly with time for one or more cycles and the corresponding variation of current is observed. The theory for straightforward processes is well established. In a reaction such as the simple one-electron redox reactions, the separation of the maxima of the peaks is related to the relative influence of activation and short term diffusion polarization. These two components tend to be lumped together in the interrupter method. Cases where the straightforward theory does not apply are usually evidenced by a lack of symmetry in the diagram. The bottom graph in this figure shows a simple method for estimating electrochemically active area through double layer capacitance determination (ref. 3). This method is especially suited to porous electrodes and is based on the existence of a potential range where electron transfer reactions do not take place to a significant extent. When this

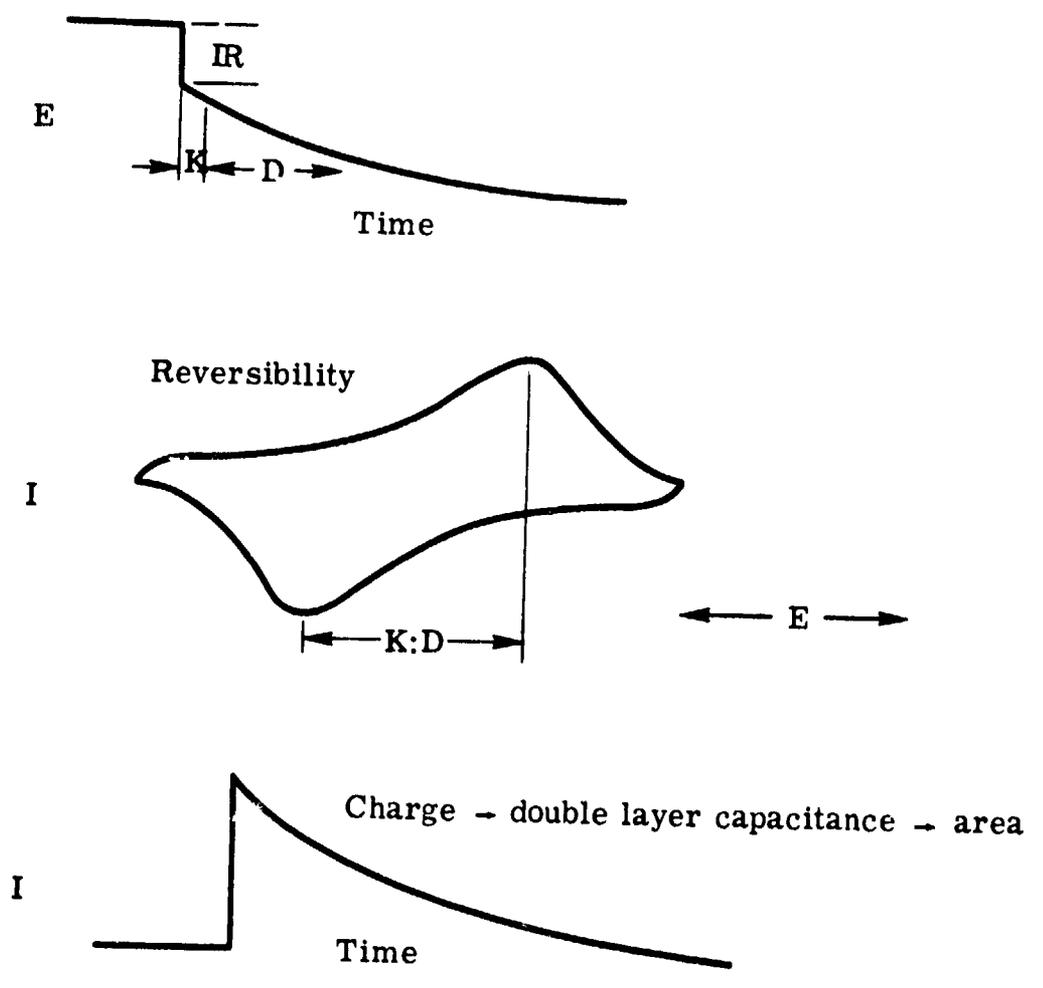


Figure 3.

is the case, a small change in voltage causes a current that is related to charging the double layer capacitance.

Contract Efforts

A follow-on effort to the "Screening of Redox Couples and Electrode Materials" contract (NAS3-19760) with Giner Inc. entitled "Investigation of Redox Couples for Energy Storage" (NAS3-20794) is only a few months old at this writing. These efforts will concentrate on the chemistry and electrochemistry of chromium solutions. Various techniques for the preparation of mixtures of chromous and chromic chloride will be investigated as will materials for the suppression of hydrogen evolution during the charge portion of the cycle.

In-house Efforts

Sweep voltammetry proved valuable in the coarse classification of the reversibility of several redox couples on various electrode surfaces. The schematic of the electronic circuit used, as well as the potential (volts vs saturated calomel electrode) vs current density curve for the ferrous/ferric reaction on a carbon cloth electrode, is depicted in figure 4. This reaction is typical of one that closely approaches being fully reversible. Figure 5 is typical of one that shows some activity but is rather irreversible. This curve was generated while testing boron carbide as an electrode for the chromous/chromic reaction. Although there is a slight oxidation peak ($\text{Cr}^{+2} \rightarrow \text{Cr}^{+3} + e^-$) the reduction peak, if any, ($\text{Cr}^{+3} + e^- \rightarrow \text{Cr}^{+2}$) was obscured by hydrogen evolution ($\text{H}^+ + e^- \rightarrow 1/2 \text{H}_2 \uparrow$). When sweep voltammetry was applied to the chromous/chromic couple in the dilute solutions ordinarily used for this technique (10^{-2} N) no peaks were observed. No carbon or graphite substrate was found on which the chromium reaction was even partially reversible. The ideal catalyst for this reaction would suppress the hydrogen evolution reaction as well as speed up the chromium reactions. The ideal half cell potential for chromium is 0.4 V negative with respect to the hydrogen evolution reaction.

Cyclic voltammetry applied to the titanium couple that had been of interest for use in redox cells revealed a long-term effect that suggested the reaction was inhibited by a surface coating. In the Cell Component Screening task, oxidized tungsten 3 percent rhenium proved to be a very reversible electrode for the $\text{Ti}^{+3}/\text{TiO}^{+2}$ reaction. Table 10 gives a brief overview of several other redox couple/electrode combinations that were evaluated using this technique.

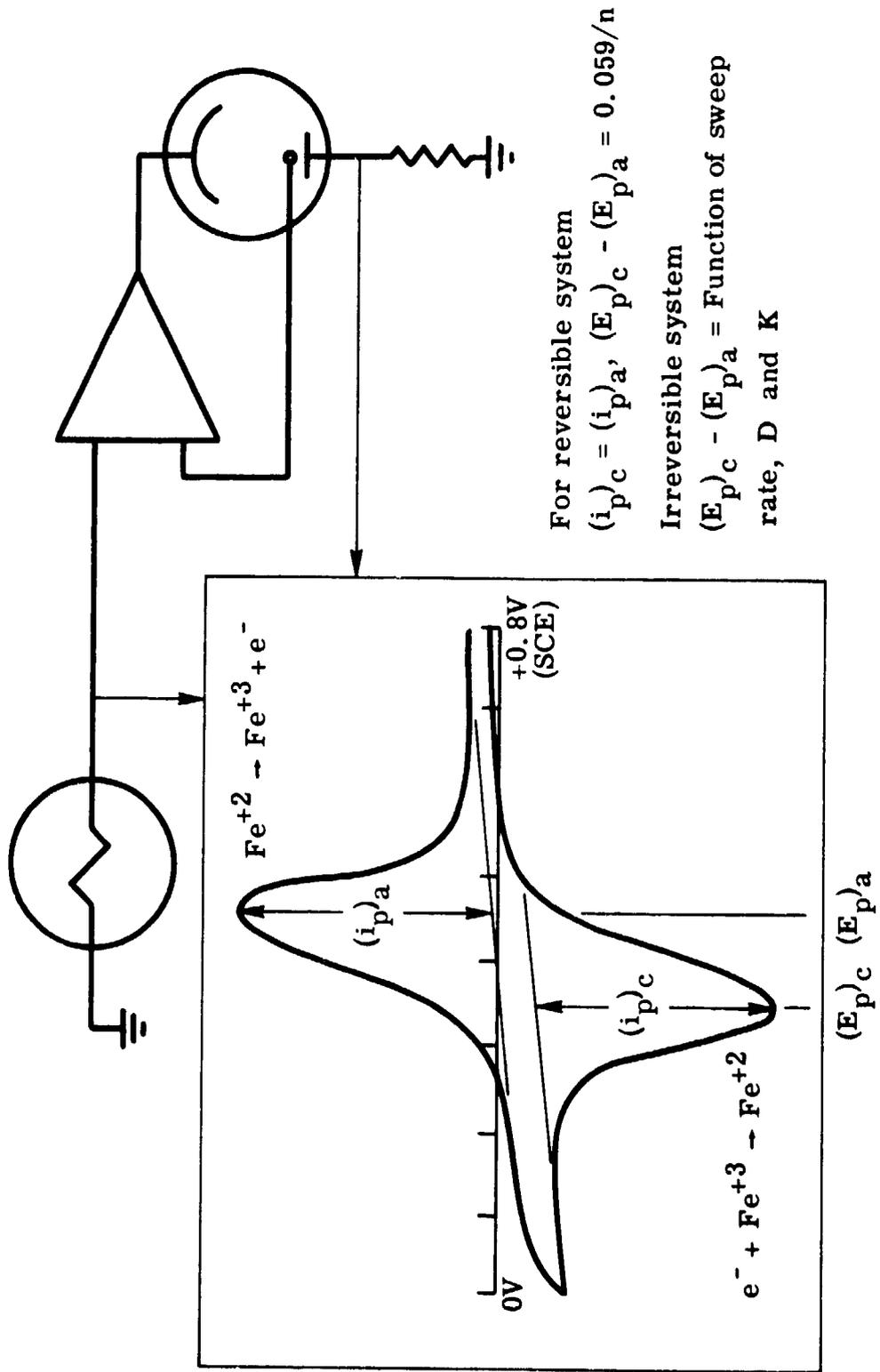


Figure 4. - Sweep voltammetry for electrode/couple screening.

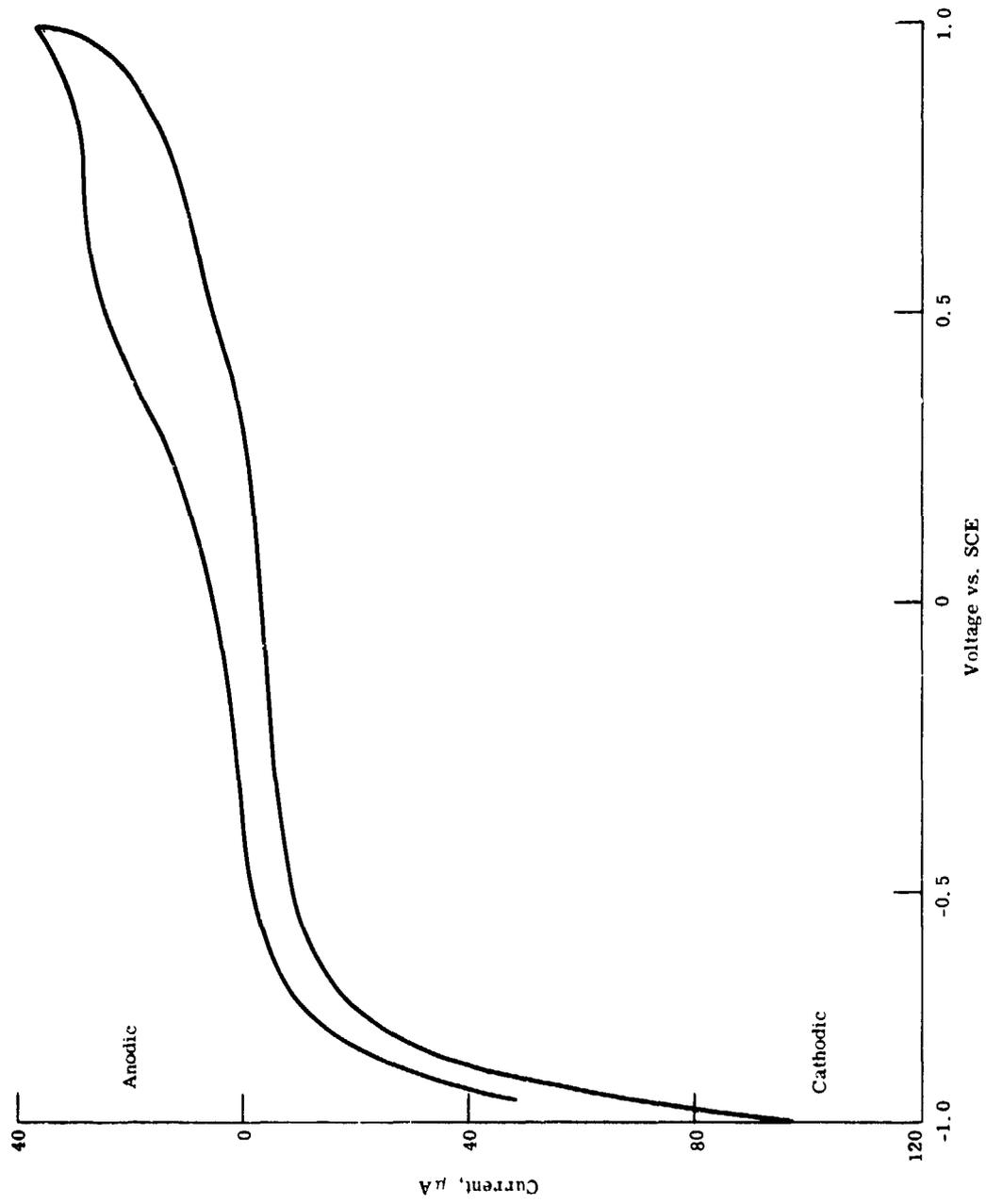


Figure 5. - Boron carbide electrode 0.7 cm diam, 0.38 cm² area 1M Cr Cl₃ in 0.5 M HCl sweep rate 20 mV/sec.

TABLE 10. - SCREENING OF COUPLES AND ELECTRODES USING
CYCLIC VOLTAMMETRY

$\text{Fe}^{+2/+3}$, on C, most reversible
 $\text{Cr}^{+2/+3}$, on C, quite irreversible
 on B_4C , small improvement over C
 $\text{V}^{+2/+3/+4/+5}$ (attractive because with wide range of E_0 values one could
 have all V system)
 $\text{V}^{+4/+5}$ and $\text{V}^{+3/+4}$, generally irreversible
 $\text{V}^{+2/+3}$, on B_4C , better than $\text{Cr}^{+2/+3}$
 $\text{Fe}(\text{O})_3^{-3}/\text{Fe}(\text{O})_3^{-4}$ on Pt - very reversible
 on C - less reversible
 low solubility of ferrous species
 $\text{Br}^-/\text{Br}_3^-$, on B_4C , indications are that this fairly reversible couple
 can be used on B_4C , thus avoiding complications of halogen interaction
 with graphite

When electrochemical active area measurements were made and compared with estimates of the true surface area it was found that the electrochemical area was much less than the true surface area, indicating that all the surface contained within the cloths, felts, and foams was not contributing to the active area. Diffusional processes in these high-tortuosity materials thus drastically reduce the effectiveness of the internal surface of typical electrode structures.

IV. CELL COMPONENT SCREENING

Introduction

Cell component screening, as the name implies, is the first level of testing that is performed on candidate electrodes, membranes, redox couples, cell materials, cell flow configurations, etc. It is in these tests that candidate components are first assembled into redox flow cells for short duration testing. The type of equipment used for this testing is shown in figure 6. These lab cells have an active area of 14.5 cm^2 (1.5 in. by 1.5 in.). The fluids are pumped around using either a nitrogen lift pump or a reciprocating bellows pump. Usually the system is charged with solutions that are 1 molar in the cation of interest and the capacity is about 1.0 A-hr. The systems are constructed of glassware and plastic tubing, and stoppered to minimize any air intrusion. These cells are cycled from full charge to full discharge for the duration of the test. Table 11 lists the membranes, electrode materials and redox couples that have received some testing during this reporting period. Figure 7 explains the terminology used with regard to the electrodes. In sum, an electrode structure which may or may not be catalyzed is placed in contact with the redox solution. Since redox couples that received the most attention this period ($\text{Cr}^{+2}/\text{Cr}^{+3}$ and $\text{Ti}^{+3}/\text{TiO}^{+2}$) are both irreversible on carbon and graphite electrodes, higher surface area materials were investigated, as well as materials on which these reactions would be more reversible. The ferrous/ferric couple, on carbon and graphite electrodes, was reversible when tested in half cells; so, in data from complete cells, evidence of irreversible behavior is attributable to the negative couple.

Redox Couples

The baseline redox couples at the beginning of this reporting period were $\text{Fe}^{+2}/\text{Fe}^{+3}$ for the positive side and $\text{Ti}^{+3}/\text{TiO}^{+2}$ for the negative side. The $\text{Cr}^{+2}/\text{Cr}^{+3}$ couple was viewed as attractive from a cost, availability, and half-cell voltage point of view but irreversible (slow) from a performance point of view. The couples that were screened were $\text{V}^{+2}/\text{VO}^{+2}$, $\text{Br}^-/\text{Br}_3^-$

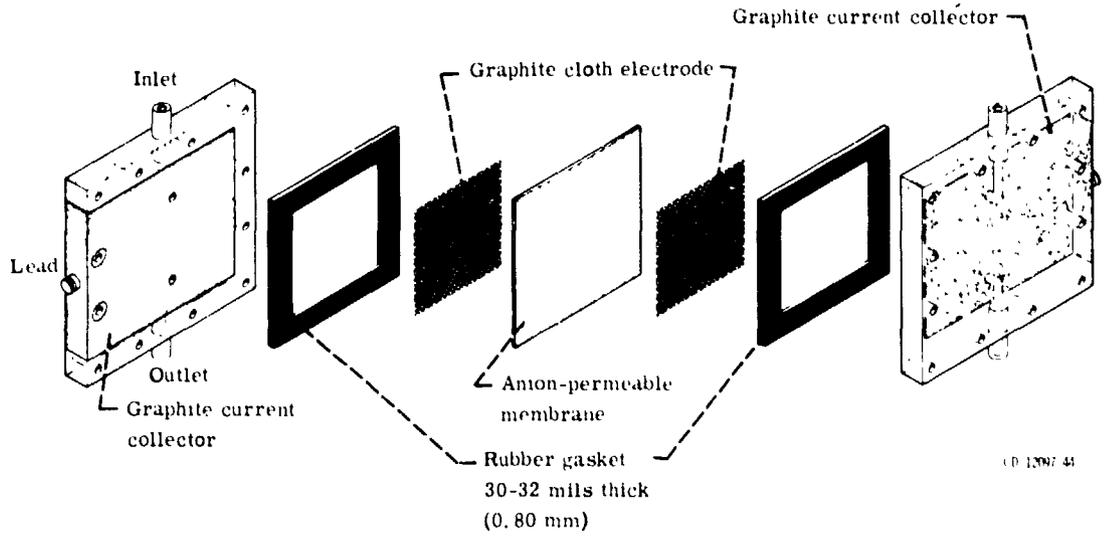


Figure 6. - Configuration of laboratory redox cell.

TABLE 11. - COMPONENTS SCREENED IN 14.5 cm² REDOX CELLS

Couples		Membranes	
Fe ⁺² /Fe ⁺³	V ⁺⁴ /V ⁺⁵	CP4L-A2-1	103-QZL-A2-3
Ti ⁺³ /TiO ⁺²	Br ⁻ /Br ₃ ⁻	CP4L-A3-1	103-QZL-B2
Cr ⁺² /Cr ⁺³	Cu(NH ₃) ₂ ⁺¹ /Cu(NH ₃) ₄ ⁺²	CP4L-A3-2	103-QZL-B10
V ⁺² /VO ⁺²	Fe(O) ₃ ⁻³ /Fe(O) ₃ ⁻⁴	CP4L-A3-3	A3L-A5-2
		CD1L-A5-3	A3L-B7
		CD1L-A5H-10	

Media - primarily acidified chloride solutions

Electrodes

Graphite cloth	Ag screen	Bi granules
Graphite felt	AgCl screen	Ti chips
Graphite foam	Hg-Ag screen	Nb screen
Reticulated vitreous carbon	Pb granules	Ta screen
Carbon chips	Hg-Pb granules	W-Re screen
		Hg-Cu screen

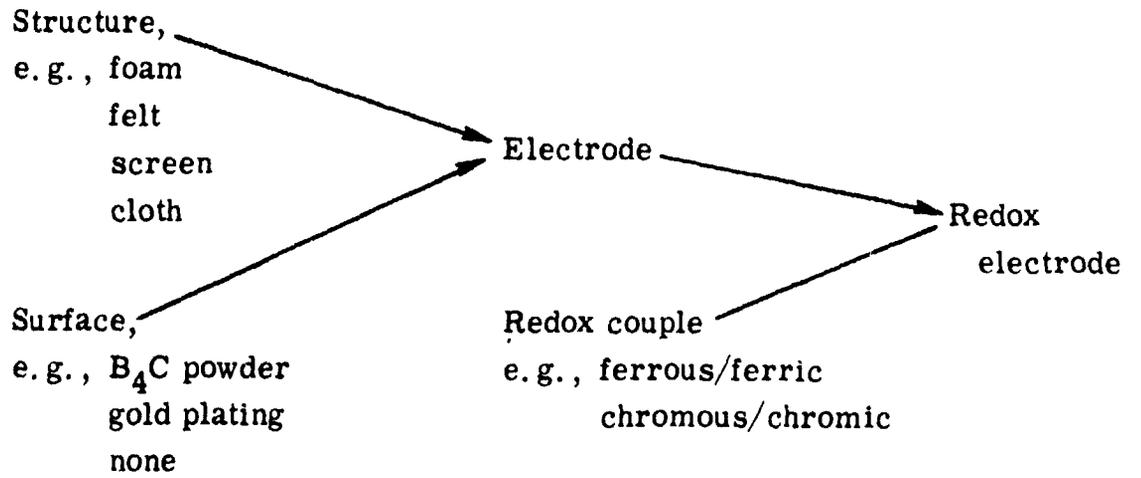


Figure 7. - Factors to be considered in fabrication of Redox electrode.

and V^{+4}/V^{+5} . Figure 8 points up the problem with the V^{+2}/VO^{+2} couple, which undergoes a valence change of two. The first step is reasonably reversible, but the second is highly irreversible on the graphite felt electrodes used. The V^{+4}/V^{+5} couple yielded a very slow reaction. Considering the high cost of vanadium chemicals, these couples were dropped from consideration. The bromide/tribromide couple is well known as a good one.

Electrodes

The baseline electrode structure during this period was a woven cloth of either carbon or graphite. As stated earlier, this was a poor electrode for the Ti^{+3}/TiO^{+2} and Cr^{+2}/Cr^{+3} couples. There were indications that a surface poisoning reaction took place when the titanium couple was used. When the chromium couple was used the coevolution of hydrogen limited the rates of charge (reduction of chromic ion) to only a few milliamperes per cm^2 ($i_0 = 0.1 \text{ mA/cm}^2$ on carbon). Figure 9 presents the results of an iron/chromium cell run to evaluate a graphite foam as the chromium electrode. The loss of capacity with cycling is typical of cells with high rates of hydrogen evolution during charge. This material was the best carbon or graphite material tested, but the capacity loss was unacceptably high.

Noncarbon or graphite surfaces were investigated in an attempt to find a more reactive surface for the chromium reactions. Figure 10 shows a charge and discharge cycle of an iron/chromium redox cell using amalgamated lead as the chromium electrode. This choice of material (and others tested) was to evaluate surfaces that were believed to have high hydrogen overvoltages. The ampere-hour efficiency was higher than with the graphite cloth electrode at comparable current densities. Power outputs were also typically higher, but the fact that the lead dissolved during discharge was undesirable: The chromous ion generated on charge reacted with lead ions, forming small particulates of lead which eventually clogged the cell.

High ampere-hour efficiencies (>95 percent) over extended cycling was possible only using graphite electrodes at low current densities (3 asf at 50 percent of charge) during the charge cycle. Typically, the charge voltage is set at 1.2 V and the current tapers during the course of charge.

For the titanium couple (Ti^{+3}/TiO^{+2}), it was found that oxidized screens of an alloy of 97 percent tungsten-3 percent rhenium were much more reversible than graphite products. Figure 11 compares the performance of a redox flow cell using the oxidized W-3 Re with cells using graphite products. A 1.0Ω load was used in all three cases. Figure 12 is a plot of the cell capacity vs the square root of the time. The recovery of some of the capacity loss by the ad-

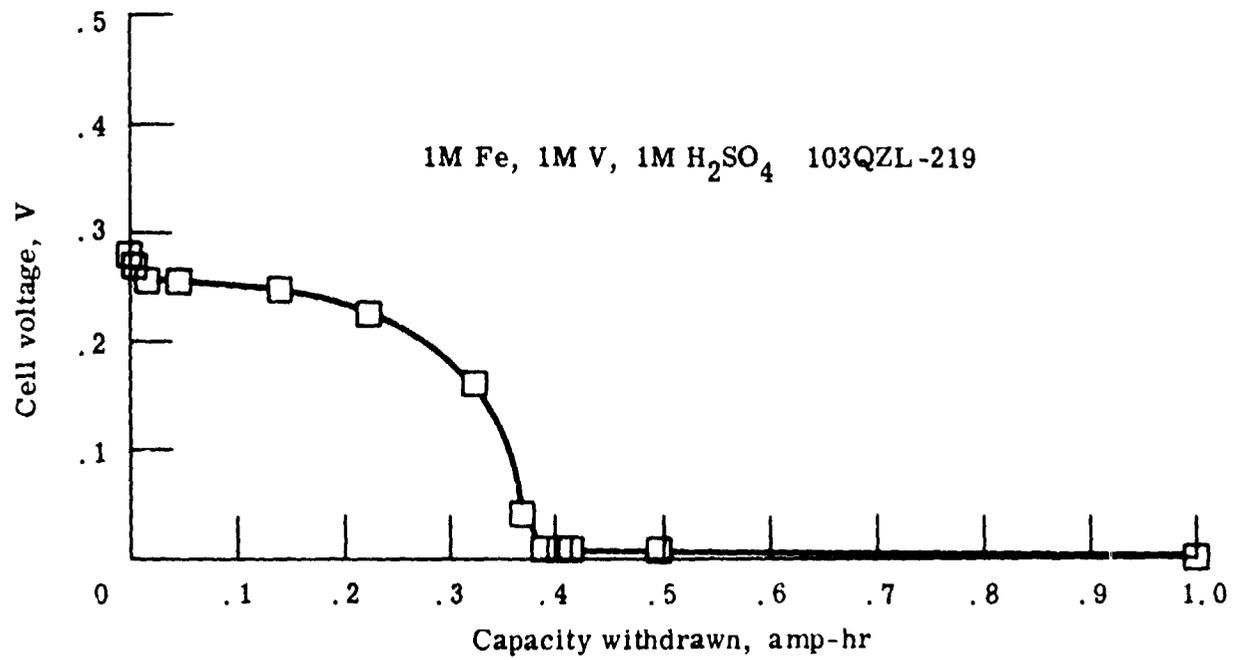


Figure 8. - Discharge characteristics of V⁺²/VO⁺² couple versus Fe⁺³/Fe⁺² using graphite foam electrodes.

Best of carbon electrodes for $\text{Cr}^{+2}/\text{Cr}^{+3}$
 Loss of cell capacity due to H_2 evolution at chromium
 electrode on charge

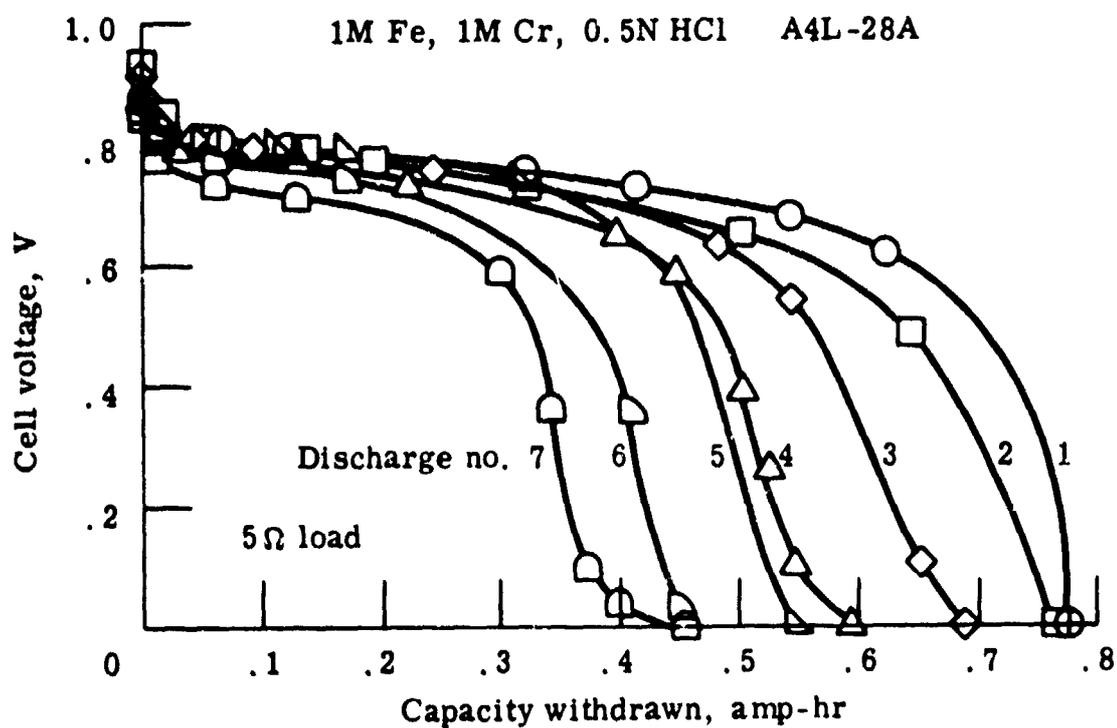


Figure 9. - Discharge characteristics of $\text{Cr}^{+2}/\text{Cr}^{+3}$ couple on graphite foam versus $\text{Fe}^{+3}/\text{Fe}^{+2}$ on graphite cloth.

Comparatively good charge and discharge performance
 Amp-hour efficiency above 90% for first six cycles
 Eventual clogging due to fine lead particles

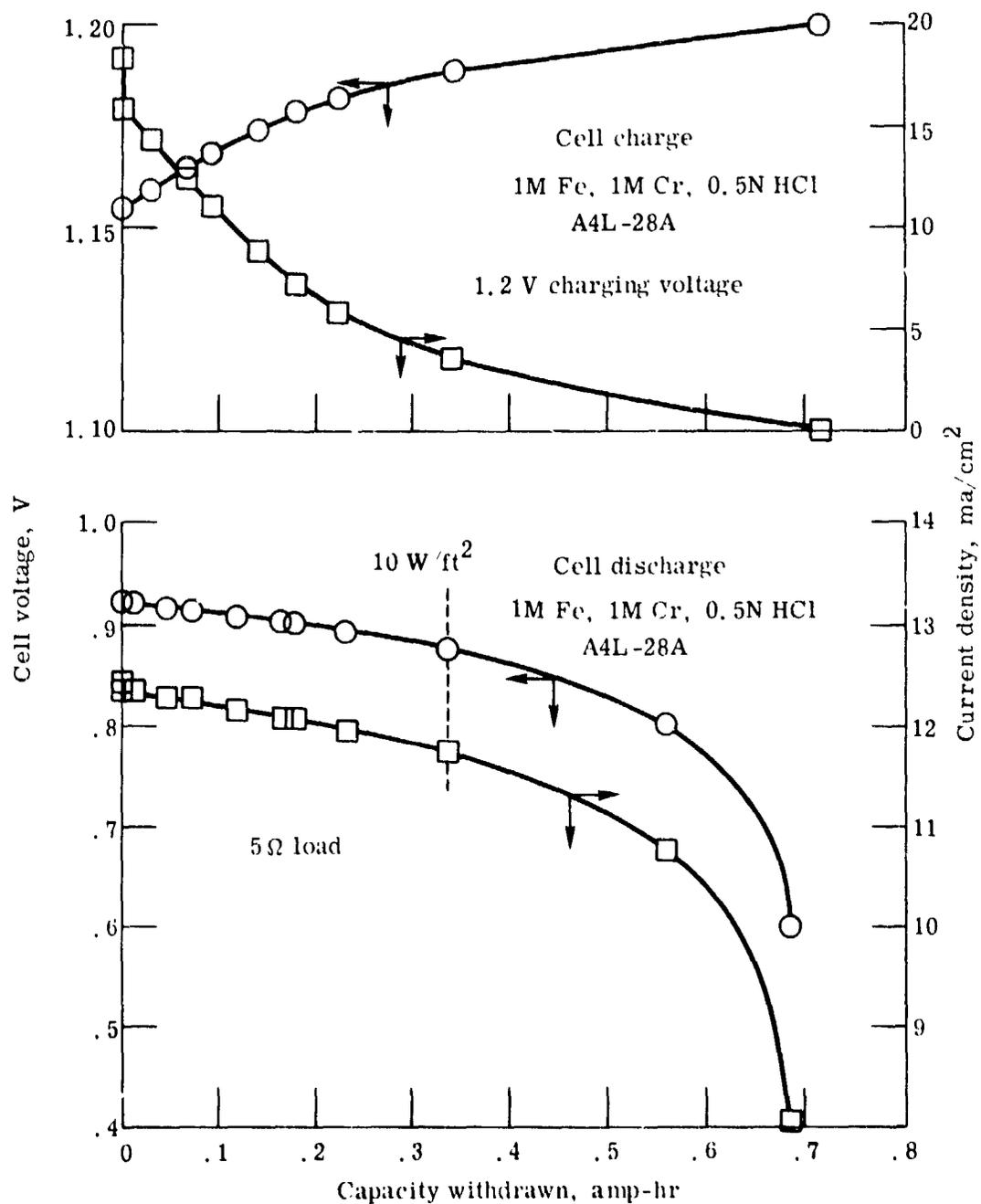


Figure 10. - Charge/discharge characteristics of $\text{Cr}^{+2}/\text{Cr}^{+3}$ couple on amalgamated lead electrode versus $\text{Fe}^{+2}/\text{Fe}^{+3}$ on graphite cloth.

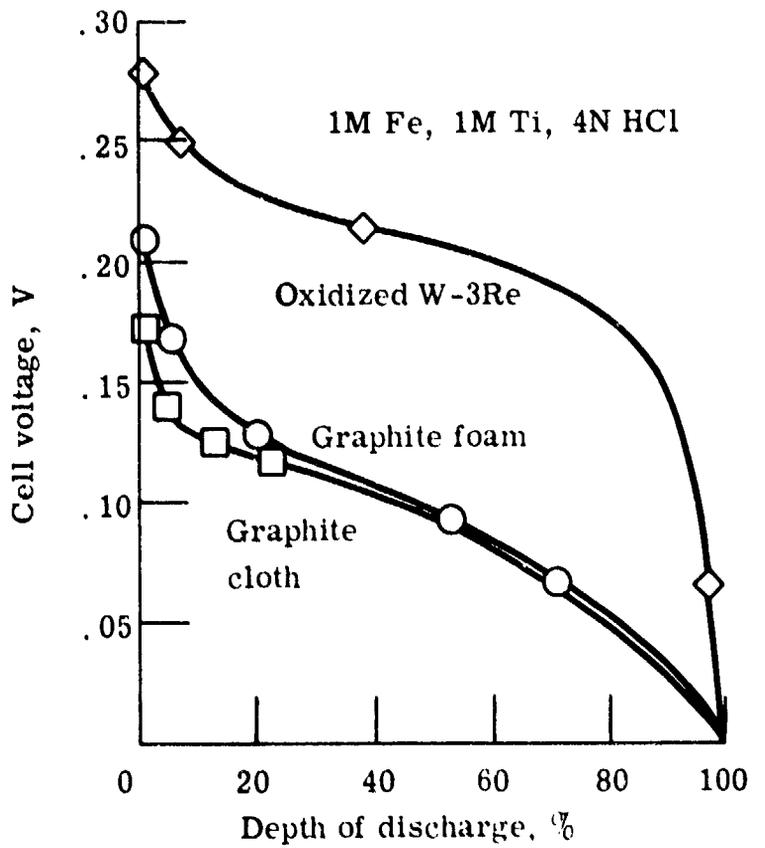


Figure 11. - Performance of oxidized tungsten-3% rhenium electrode compared to graphite foam and cloth electrodes.

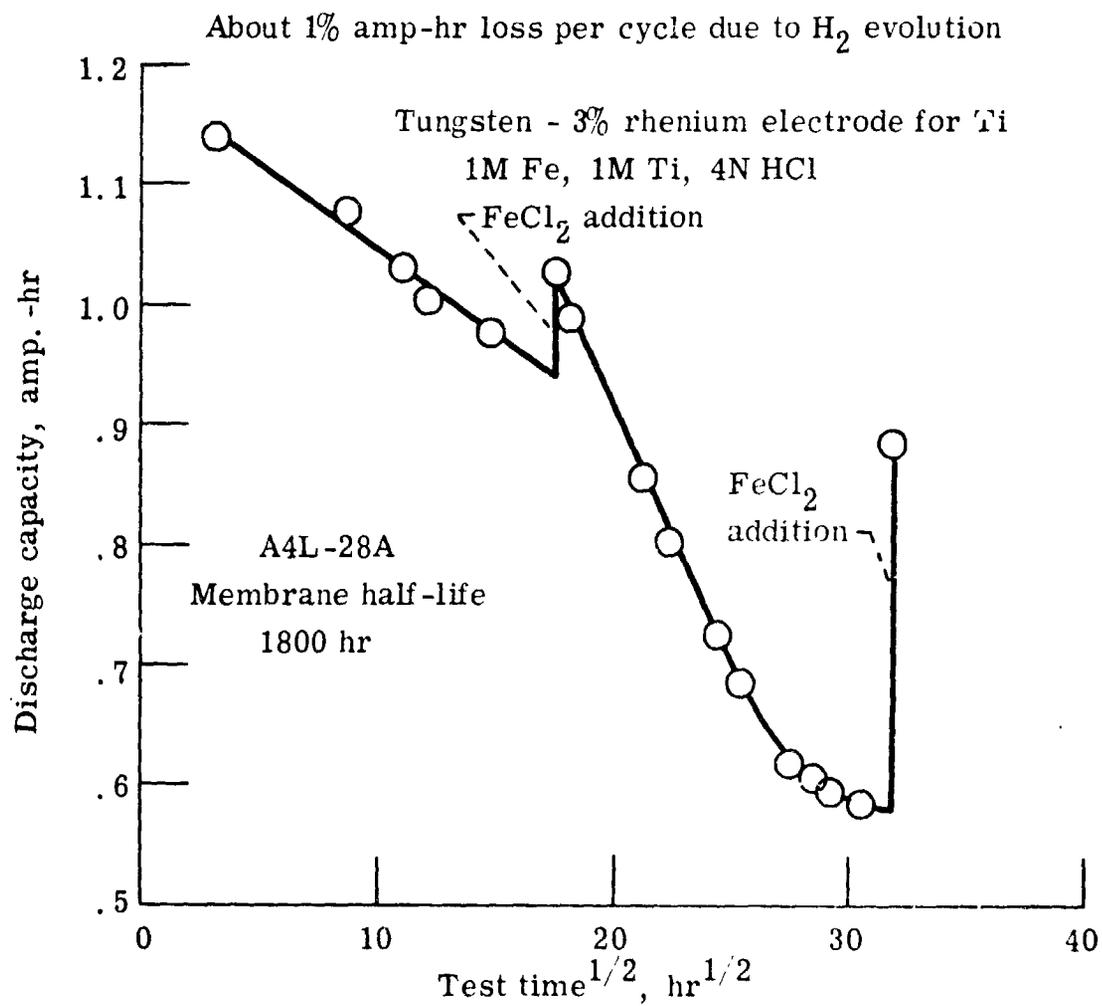


Figure 12. - Cell capacity as a function of test time.

dition of ferrous chloride to the positive side of the system is indicative of charge imbalance between the titanium and the iron solutions. In this cell, this imbalance was attributed to the coevolution of hydrogen during recharge. It was estimated to be about 1 percent loss of capacity per cycle. This W-3 Re alloy was found to be the best of the different materials screened for use as titanium electrodes.

The power output of an iron/chromium cell using W-3 Re screen electrodes is shown in figure 13. A maximum of 38 W/ft^2 was delivered at a cell voltage of 0.52 V. The poor hydrogen overvoltage characteristics of the W-3 Re precluded any possibility for recharging the cell using this material. When used in an iron/titanium cell a maximum of 19 W/ft^2 were delivered at a cell voltage of 0.33 V (fig. 14).

V. SYSTEM CONSIDERATIONS

System Studies

During calendar year 1976 two redox system computer models were developed under contract by Exxon Corp. (ref. 4). The first of these, referred to as the Stage 1 model, assumes time-averaged values for all system parameters such as voltage, power level and electrolyte concentrations. The second model, referred to as Stage 2, was to handle any charge/discharge power profile, and to take into account the effect of time-dependent reactant concentrations on electrochemical parameters (polarizations, current density, etc.) and the effect of hydrodynamic considerations on cell mass transport.

In its delivered form the computer program for this latter model contained many errors of both programming and algorithmic types. Most of the limited in-house effort expended on system studies in 1977 was used to correct these errors and put the program into a useable form. The most serious error uncovered (which also applies to the Stage 1 model) was that several of the subroutines for calculating the costs of certain system components were generating excessively high numbers. Reevaluation of these subroutines by Exxon Corp., plus an independent study by a local engineering design company, confirmed that the calculated filter costs were too high by a factor of 4-10 and the calculated pump costs were too high by a factor of about two. These corrections, when applied to the Base Case system design using the Stage 1 model (ref. 1), result in a decrease in calculated system cost (\$/kW) of about 35 percent. This represents a considerable improvement in the projected economic viability of redox systems for utility storage.

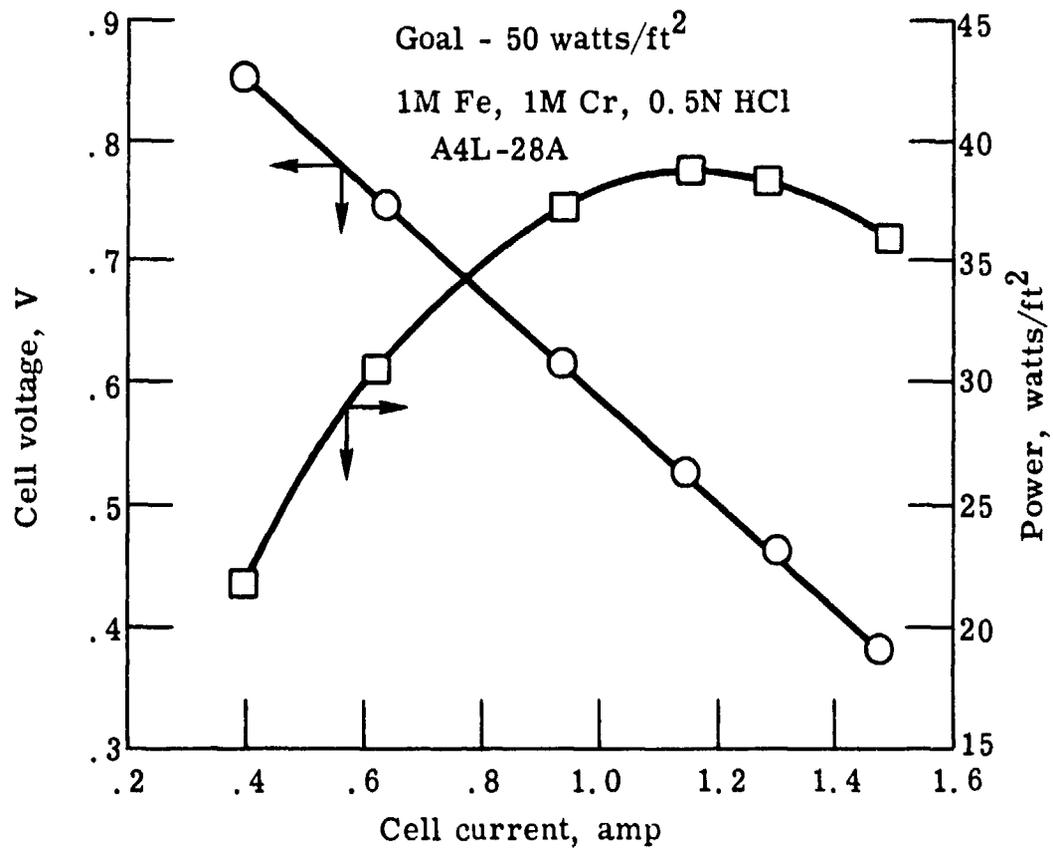


Figure 13. - Power output of an iron/chromium cell with oxidized tungsten-3% rhenium electrodes.

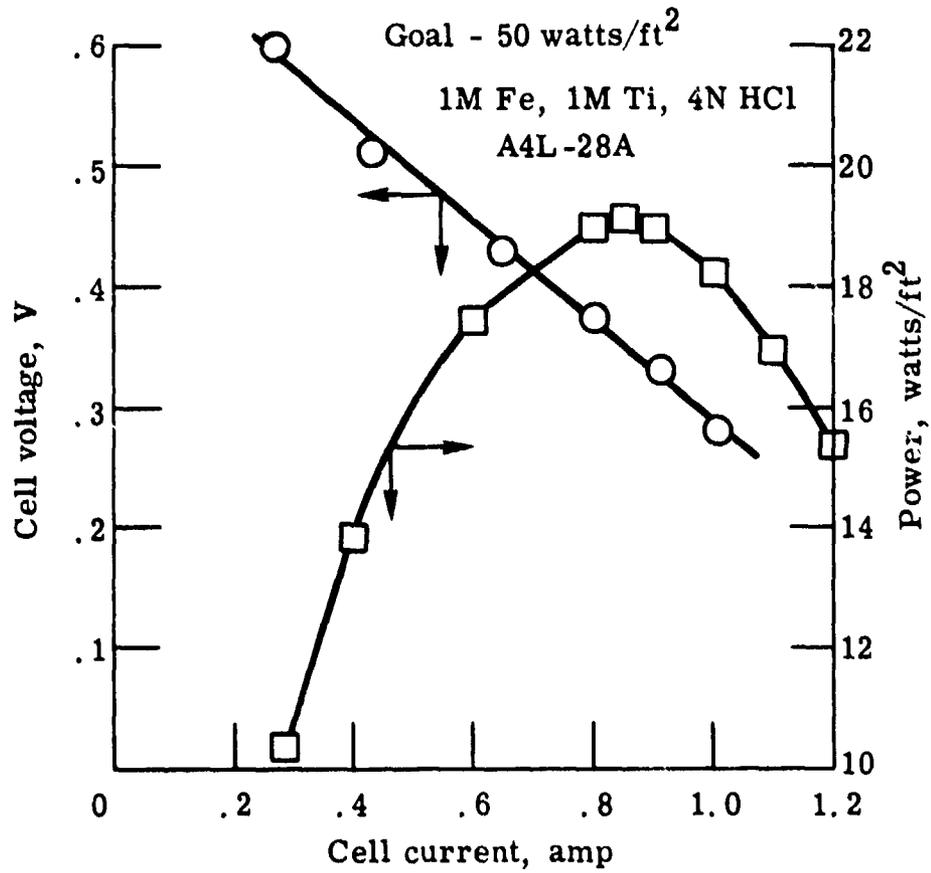


Figure 14. - Power output of an iron/titanium cell with oxidized tungsten-3% rhenium electrode.

Materials Availability

A brief study was made of the world-wide resources for the raw materials which are sources of the redox reactants of primary interest at Lewis. In table 12, which presents the results of this study, "Resources" refers to total known raw material deposits which could be mined, while "Reserves" refers to ore which can be mined economically at today's market prices. Roughly speaking, reserves are about one-third of resources for these materials. The results of this study indicate that the installation of 100, 100 MWhr redox storage systems would not greatly tax the production capacity for ores of iron or chromium. However, if titanium and bromine were to be used as redox reactants, requirements would make a significant impact on the present production.

Redox System Hardware

Although there is not at present any large-scale production of redox systems, per se, there does exist considerable commercial production of systems which have much in common with redox systems. For example, Ionics, Inc. markets a water desalination unit which utilizes alternately-stacked anion and cation exchange membranes and an applied electric potential to separate salts from a sea water or brackish water feed stream. A typical unit, shown in figure 15, is largely of plastic construction and contains most of the components required by a redox system. In principle, all that would be required to convert this unit into a redox system would be reactants, tankage, intra-cell electrodes and, if necessary, heat exchangers. Much of the membrane preparation and cell stacking for this unit presently is performed by hand, so there exists a considerable potential for cost reduction through automation. In short, there is in place at this time the technology and the production capability for the commercialization of redox systems.

Typical stack components such as membranes, end plates and flow field spacers are being purchased from Ionics, Inc. These will be incorporated into redox cell stacks for testing and evaluation in 1978.

Redox System Cost Projections

In order to gain some perspective on the ultimate possible cost for redox systems, the following assumptions were made:

- (1) The present cost per square foot of membrane area of an Ionics, Inc. desalination system can be reduced from \$20-25/ft² to \$10/ft² by automation of manufacturing and assembly;

TABLE 12. - SUPPLY AND COST OF RAW MATERIALS FOR POSSIBLE REDOX REACTANTS

{ Data in million short tons. }

Reaction	Raw material	Principle raw material location	Resources		World reserves	1976 Production		1976 Raw material price \$/short ton	Percent ^a of 1976 world production	Ore cost \$/1000 Ahr
			World	U. S. A.		World	U. S. A.			
Fe	Iron ore	Worldwide	$8.96 \cdot 10^3$	$121 \cdot 10^3$	$285 \cdot 10^3$	987	90	18	0.0094	0.08
Cr	Chromite ore	S. Rhodesia S. Africa	$18 \cdot 10^3$	8	$2.7 \cdot 10^3$	9.49	W ^b	d ³⁵	1.6	.25
Ti	Ilmenite ore ^c	S. Africa Canada U. S. A.	$3.70 \cdot 10^3$	574	771	4.28	0.652	49	2.0	.30
Br	Rutile ore ^c	Australia	220	6	176	.440	W ^b	510	15.5	1.67
	Sea water Brine wells	Worldwide	Virtually unlimited		Unknown but large	.327	0.220	600	31.4	2.97

^aBased on one hundred, 100 MWhr plants/year.^bInformation withheld.^cAs concentrate. Ilmenite: 54 percent TiO₂; Rutile: 100 percent TiO₂.^dSouth African ore.

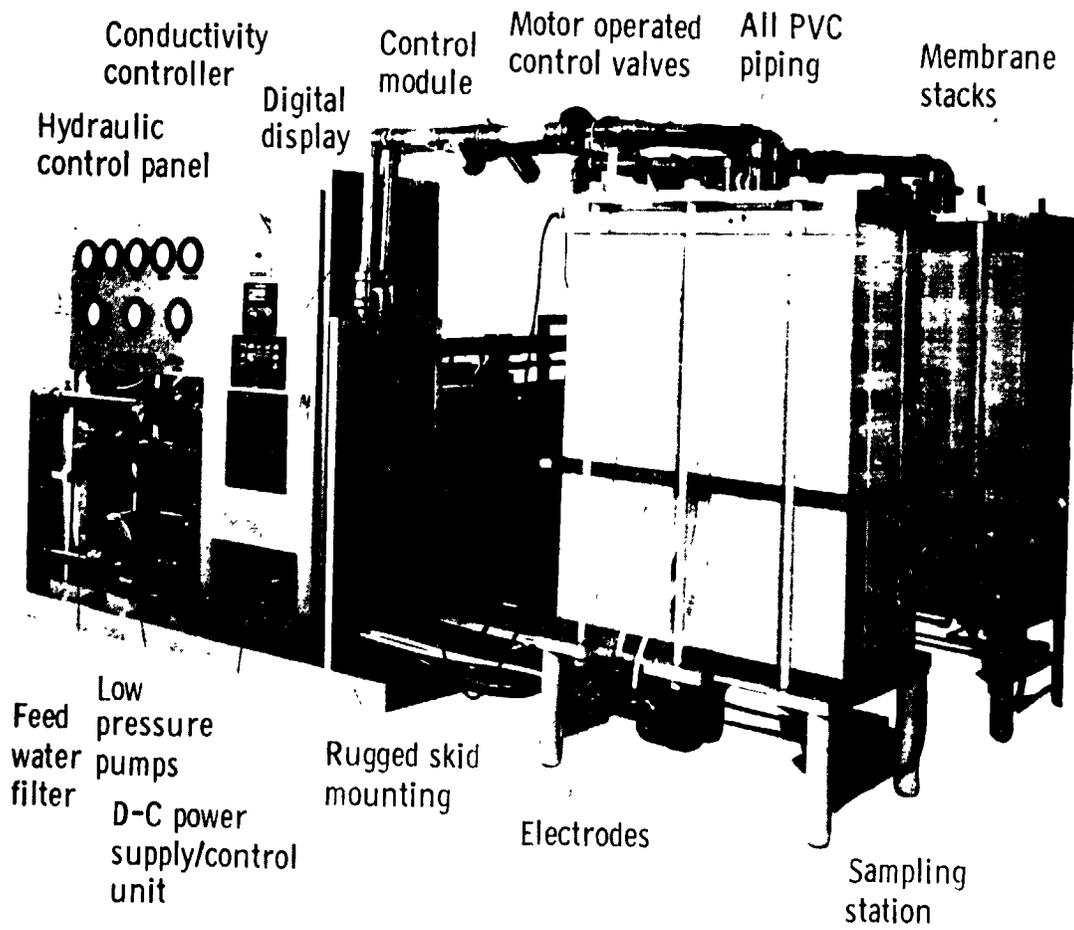


Figure 15. - REDOX-type hardware now in use, unit manufactured by Ionics, Inc..

- (2) The cost for electrodes will be \$4/ft²;
- (3) The cost for reactants will be \$5/kWhr;
- (4) The cost for tankage will be \$5/kWhr;
- (5) The cells will operate at 100 W/ft².

Under these assumptions, total redox system cost becomes \$140/kW plus \$10/kWhr. In table 13 this projected cost for a redox system is compared with projected costs for lead-acid and high-temperature batteries for two possible storage applications. This table indicates that, if the above assumptions become realities, a redox system represents a storage device of definite economic feasibility.

REFERENCES

1. An Assessment of Energy Storage Systems Suitable for Use by Electric Utilities, Vol. II. Public Service Electric and Gas Co., Newark, N. J., 1976. (See also Electric Power Research Institute, EPRI-EM-264 Vol. 2.)
2. Alexander, S. S.; and Hordson, R. B.: Anion Permselective Membranes. CONS/0108-1 NASA CR-135316, (Ionics, Inc.; NASA Contract NAS3-20108 and Dept. of Energy Contract E(49-28)-1002) 1978. (See also CONS/0108-1.)
3. Seiger, Harvey N.: Sinter of Uniform, Predictable, Blemish-Free Nickel Plaque for Large Aerospace Nickel Cadmium Cells. (Heliotek, NASA Contract NAS1-10694.) NASA CR-132481, 1975.
4. Ciprios, G.; Erskine, W., Jr.; and Grimes, P. G.: Redox Bulk Energy Storage System Study. (EXXON/GRU.1BH.77-vol. 1 and EXXON/GRU.2BH.77-Vol. 2, Exxon Research and Engineering Co.; NASA Contract NAS3-19776.) NASA CR-135206, 1977 and Ciprios, G.: Final Report Corrigendum, Feb. 28, 1978.

TABLE 13. - COMPARISON OF PROJECTED REODX SYSTEM COSTS
WITH PROJECTED BATTERY SYSTEMS COSTS

Lead acid battery	\$50/kWhr + \$40/kW for power processing
High temperature battery	\$30/kWhr + \$40/kW for power processing
Redox	\$10/kWhr + \$140/kW

Bulk storage application - 10 MW for 8 hr

Solar photovoltaic or wind - 1 MW for 100 hr

System	System costs	
	Bulk storage	Solar/wind
Lead acid	$\$4.4 \times 10^6$	$\$5.04 \times 10^6$
High temperature	$\$2.8 \times 10^6$	$\$3.04 \times 10^6$
Redox	$\$2.2 \times 10^6$	$\$1.14 \times 10^6$